University of
Waterloo Research Institute

FINAL CONTRACT REPORT

Evaluation of the Flash Liquefaction Pyrolysis Process Applicable to Canadian Coals

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SUMMARY

The present report concludes much of the work of evaluating the atmospheric pressure fluidized bed flash pyrolysis process for the production of liquids from Canadian coals. Earlier contract reports described screening investigations of a number of Canadian coals to evaluate liquid yields from this flash pyrolysis process. Some more specific aspects of coal pyrolysis were investigated in the present work, particularly for low rank coals.

General objectives of this study were to investigate the effect of acid washing on the yields of pyrolysis liquids from lignite or sub-bituminous coal, since earlier work had shown that removal of ion exchanged cations could result in substantial improvements in liquid yields. This work formed a major part of the study. Other objectives were to evaluate the effect of steam or carbon dioxide atmospheres on the yields of pyrolytic liquids, and to carry out pyrolysis on a larger scale than in previous work (1.5 kg/hr vs. 50 gms/hr). Some tests were also planned to see if the agglomerating tendencies of caking coals in a fluidized bed could be controlled by some form of easily done pre-treatment. Reactivities of coal chars were also measured by a TGA technique.

The major conclusions of this work are summarized below in point form.

1. Tar liquid yields were substantially improved from Saskatchewan (Estevan) lignites or from Alberta (Forestburg) sub-bituminous coal by removing the alkaline earth cations associated with the organic coal matrix. These cations were removed by an ion exchange process by acid washing to a pH of 1.5 to 2.5. The improvement in tar yields, of up to 50%, depends directly on the amount of exchangeable cations per kg. of dry coal. In general, improvement in tar yield was in the order lignites > sub-bituminous C > sub-bituminous B > bituminous. The latter coal (Balmer) showed very little benefit from acid washing. Acid consumption was about 1.1 to 1.2 times the equivalent amount of cations removed. Any appropriate acid can be used e.g. HCl, H_2SO_4, H_2SO_3. The removal of exchangeable cations increased tar yield at the expense of gas yield, particularly CO_2. The gasification effectiveness of these organically bound cations was calcium > magnesium > potassium > sodium. Iron and aluminum were not exchangeable and were not removed by acid washing.

2. Acid washing of lignite or sub-bituminous coal resulted in a significant de-ashing - 60% removal for Estevan lignite and 44% for Forestburg sub-bituminous coal. Hat Creek sub-bituminous coal had a very high ash (clay) content, and benefits of acid washing were minimal. Tar product quality was about the same from raw or acid treated coal.

3. An order of magnitude estimate of the costs of acid washing a lignite coal indicate that the cost of recovery of the

incremental tar produced depends to a large extent on acid cost. With an order of magnitude allowance for processing cost of the acid washing step, for sulfuric acid at $100/t, the incremental tar costs $33/bbl. (42 U.S.gallons), for acid at $50/t, the tar costs $20/bbl., for acid at $25/t, the tar costs $14/bbl. and for waste acid the cost of the incremental tar production would be $7/bbl. No credit is taken for de-ashing. The spent acid wash solution would be inocuous and would require only some aeration to remove trace organic matter.

4. Flash pyrolysis of coal in a steam atmosphere does not appear to offer any advantage in achieving a higher tar yield; and may in fact reduce tar yields slightly because a steam-tar reforming reaction appears to occur to a small degree at optimal flash pyrolysis conditions. This conclusion agrees with work at CSIRO (Australia).

5. Lower rank coals were pyrolyzed without difficulty in a larger scale unit (1.5 kg/hr), and in particular, lignite was treated with no operating problems in our normal unit. Higher rank coals e.g. high volatile sub-bituminous coal require some modifications to product collecting systems because of the stable tar fogs formed. Other workers have found oil scrubbers or electrostatic precipitators to be more suitable than the surface condensers used in the present work. Initial tests with an electrostatic precipitator during pyrolysis of a Forestburg sub-bituminous coal gave good results.

6. Yields of tar in the larger scale unit were higher for

lignite than in the bench scale unit, but lower for sub-bituminous coal. The latter result may be in error due to product collection problems. Recycling of product gases without removal of C_2 + or BTX fractions, as was done in these tests, also reduces the yields of liquid products. It is expected that the bench scale and larger continuous unit will give the same yields at comparable operating conditions. Electrostatic precipitators or liquid scrubbers are probably necessary for liquid product collection in continuous operation.

7. Attempts to control the agglomeration of caking coals in a fluid bed reactor by pre-oxidation were successful only if pre-oxidation was extensive, and some reduction in tar yield then resulted. The free swelling index appears to be a reasonable indicator of agglomeration behaviour. Tentatively, this index should not be more than 1 to 1.5 to avoid operating problems.

Blends of caking and non-caking coals were also pyrolyzed in an attempt to control agglomeration. Again, this approach can be used if the FSI of the blend is low enough, which usually means that the blend has to contain a higher proportion of non-caking coal than of caking coal.

Work by others suggests that spouted bed operation may be able to pyrolyze coals with FSI values to 3.0 or 3.5.

8. The relative reactivity of coals or of coal chars can be readily assessed by thermal gravimetric analysis using CO_2 as the reactant gas. The effect of the presence or absence of various types of mineral content can be readily shown. Mineral cations associated with the organic coal matrix in ion exchangeable form

catalyze the reaction of coal char. Chars from lignite coal, particularly, are very reactive due to the inherent catalytic action of this type of mineral matter. When it is removed by acid washing, a much less reactive char results. Higher rank coals, in which alkali or alkaline earth cations do not exist in ion exchangeable form, give relatively unreactive chars.

9. Tests with a caking bituminous coal (Sukunka) indicate that little benefit is achieved through pyrolysis in a CO_2 atmosphere. Tar yield was not significantly increased, and agglomeration problems were not improved.

10. Pyrolysis of acid washed lignites or acid-washed sub-bituminous coals in CO did not significantly affect tar yields or product quality.

11. Measurement of the carboxylic acid content of lignite suggests that only about one half of these groups are ion exchange centres for mineral cations.

Further work in evaluating the chemical nature of liquid tar products, especially those from acid washed lignite coals, is now being undertaken.

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Evaluation of a Flash Liquefaction Pyrolysis Process Applicable to Canadian Coals

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INTRODUCTION

Chronology

Work on coal pyrolysis was initiated at the University of Waterloo in 1979 using a small bench scale fluidized bed apparatus patterned after that developed by CSIRO (Tyler, 1979). During the initial work carried out (Scott, 1980), a somewhat larger scale reactor was developed than that used by Tyler - 15 gms/hr throughput rather than 1-3 gms/hr. This larger scale was made possible by the development of a new entrained flow feeder which allowed feed rates of 5-100 gms/hr with a reproducibility of ±5% (Scott and Piskorz, 1982). In this preliminary work, the methodology and procedures were developed for the bench scale mini-fluidized bed apparatus, and a series of pyrolysis tests were done on Alberta Forestburg sub-bituminous coal which indicated that yields of liquids comparable to those obtained by others could be realized.

In June, 1981, a new program was initiated to evaluate the short residence time pyrolysis of coal at atmospheric pressure with the primary objective of determining conditions for optimum yields of liquids from a sub-bituminous coal (Scott, 1982). During this work, covering the period to June 1, 1982, the bench

scale fluidized bed method was improved so that better material balances were obtained, and a small stainless steel reactor was developed in place of the earlier quartz version. In fact, three coals were tested for pyrolysis behaviours. two Alberta sub-bituminous coals and a Nova Scotia bituminous coal.

Results from this work were sufficiently encouraging that a further program was planned for 1982/83 and funding was received on October 1, 1982. The results from this program, including a minor extension to March 31, 1984, were given in a previous report (Scott, 1984). In this work, eight Canadian coals were tested to determine optimal yields of liquids obtainable through flash pyrolysis in the atmospheric pressure fluidized bed process. Although the best tar yields were obtained with strongly caking high volatile bituminous coals, agglomeration in the fluid bed during pyrolysis caused severe operating problems. Pre-oxidation treatment prevented agglomeration but also adversely affected tar yields. Therefore, further work was proposed to be carried out on lignite and sub-bituminous coals only. In particular, the effect of acid washing of coals was to be studied, inasmuch as preliminary tests indicated significant benefits. Initial pyrolysis tests in a larger (2 kg/hr) unit were also proposed. The results of these studies are reported here.

A part of the two earlier reports (1980, 1982) has been a state-of-the-art review of coal pyrolysis research activities, particularly in North America and the Pacific. This report also

includes such a review of coal liquefaction work in Australia and New Zealand, particularly the former.

Summary of Early Work

Previous studies reported that yields of 10% - 12% (max) of hydrocarbon liquids could be obtained from Alberta Forestburg or Highvale (Wabamun) coal at optimum conditions of 650°C, one atmosphere absolute pressure in a nitrogen atmosphere and about 0.44 secs. apparent gas residence time. Both these coals are sub-bituminous, low to medium volatile in rank. Additional pyrolysis tests done on a Devco coal (high volatile bituminous caking coal) indicated that oil yields of 17% - 21% max could be obtained at temperatures from 650°-750°C and about 0.5 sec. apparent residence time. However, operating problems with the fluidized bed were also encountered due to the caking behaviour of the coal, as mentioned above.

Additional tests using the sub-bituminous coals showed that a CO_2 atmosphere seemed to have little effect in increasing liquid yields, contrary to literature reports. A hydrogen atmosphere reduced liquid yields and increased gas yields.

The major analytical problems were found to be in the accurate determination of water, and in obtaining good results for the amounts of highly volatile hydrocarbon liquids produced. However, tar yields, when normalized, appeared to agree well with those of other workers reported in the literature for coals having similar H/C ratios.

More extensive pyrolysis tests of eight Canadian coals followed this earlier work. The main conclusions of this screening program, as reported in full earlier (Scott, 1984), are summarized below. Some of the results for low rank coals have also been accepted for publication (Scott et al., 1986).

1. The fluid bed flash pyrolysis process exhibits an optimum temperature for maximum liquid yield. This temperature is from 600°-650°C for low rank coals and 650°-700°C for higher rank coals. The maximum tar yield for Canadian bituminous coals can be predicted from the CSIRO correlation of parent coal H/C ratio vs. maximum tar yield. Tar yields from lower rank coals are not yet predictable, and are not related to the volatile yield of a proximate analysis.

2. The tar and char products from low rank coals show a decreasing atomic H/C ratio as temperature increases. The H/C ratios for bituminous coal tars and chars remain reasonably constant with temperature.

3. For both low rank and high rank coals the shortest residence time gave the highest liquid yields (0.2 to 0.45 seconds).

4. The minimum particle size for good liquid yields from fluidized beds appears to be about 100 µm. However, this will be a function of reactor configuration, operating mode and heat transfer capabilities.

5. Accumulation of char in the reactor does not affect liquid yields providing the char is not activated at high temperatures (above 900°C). The use of a CO_2 atmosphere does not appear to improve liquid yields for a coal previously exposed to CO_2. However, a fresh, unoxidized coal might show some effect - this has yet to be determined.

6. The use of a hydrogen atmosphere and a Co-Mo de-oxygenation-hydrogenation catalyst as the fluid bed material did not improve tar yields for lower rank coals. However, catalytic effects were evident, so that a different choice of catalyst might prove to be beneficial.

7. Quenching of the reaction products with a flow of cold gas did not improve liquid yields in this reactor. The reasone are not clear, but may be due to higher gas velocities in the reactor.

8. Acid washing of a lignite to remove cations associated with the organic matter, followed by pyrolysis, gave a dramatic increase in maximum tar yield - about 50%. The acid washed lignite gives a tar yield in agreement with that predicted from CSIRO and U.S. results for acid washed lignites or brown coals.

9. Pre-oxidation of a strongly caking bituminous coal prevents agglomeration and caking in the fluidized bed. Without such pretreatment, operating problems due to caking of the bed solids may arise. However, pre-oxidation of the coal also causes a significant decrease in tar yield. Some optimum level of treatment should exist.

10. In general, Canadian coals, especially those from Western Canada, have low H/C ratios compared to coals of similar rank from other sources. Low H/C ratios can be correlated generally to lower tar yields. The highest tar yields were obtained from high volatile bituminous coal, (16-20%), or from acid washed lignite (12-14%). The lowest tar yields were obtained from low volatile bituminous coal, or from high ash sub-bituminous coals (5-7%). The range of tar yields from lignite, sub-bituminous coals or medium volatile bituminous coals is from 10-14% (all yields maf).

11. Chars produced in the pyrolysis process, particularly those formed at the lower temperatures, are very reactive. There is strong evidence that they rapidly adsorb oxygen and water from the air even on short exposure.

12. Future studies on pyrolysis of coals should use dry feeds, and chars should be kept in a dry inert atmosphere as much as possible, if good material balances and good analytical results are desired.

13. The fluidized bed reactor appears to be a very suitable device for the pyrolysis of lignite or subbituminous coals. No operating problems were encountered in the bench scale unit and product yields were about the same as those obtained by others. The "blow-through" method of operation used in the Waterloo Flash Pyrolysis process for biomass appears to be feasible also for low rank coals, so that transport of heat carrying sand is not necessary and a single fluidized reactor with an independent heat source can be used.

From the above summary, the most promising areas for further work appeared to lie in investigations of the effects of inorganic cations on the yield of liquids from lignites or subbituminous coals, in attempts to improve fluid bed performance with bituminous coals, and in assessing operation of a larger pyrolysis unit. In addition, steam as a reaction atmosphere was of some interest.

OBJECTIVES OF PRESENT WORK

The primary objectives of the present work were to evaluate in more detail some additional aspects of the flash pyrolysis process for lower rank Canadian coals, especially Saskatchewan lignites. In addition, some processing alternatives for caking bituminous coals were of interest.

Specific objectives originally proposed were as follows

1. To investigate the effect of acid washing to remove cations associated with the organic matter in lignite or sub-bituminous coals. Different acids were proposed (HCl and H_2SO_4). Optimal conditions were to be determined.

2. To pyrolyze acid-washed coals to determine the effect of cation removal on liquid yields, and insofar as possible, on liquid product quality, for optimal acid-washing.

3. To carry out further pyrolysis tests of lignite and a higher rank coal in CO_2 atmospheres.

4. To carry out pyrolysis tests of lignite, sub-bituminous and bituminous coals in a steam atmosphere.

5. Some tests on a bituminous caking coal using different sand/coal particle ratios, different fluidization velocities and different feed rates to determine if agglomeration could be minimized or prevented.

6. Tests in a larger unit (2 kg/hr) for lignite, sub-bituminous and bituminous coals.

7. Presentation of results at 2nd Coal Liquefaction Contractors Review Meeting (November, 1984).

All the above objectives were achieved to a greater or lesser degree. Attempts to control agglomeration of caking coals were disappointing, so more extensive work was carried out on the acid washing technique, and on the effect of the inorganic cations on yields of pyrolytic liquids. The data presented reflect the relatively greater effort made in the study of the effects of cation removal by acid washing.

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MATERIALS AND PROCEDURES

Introduction

Details of the bench scale fluidized bed apparatus have been given in earlier reports. In the present work, two reactor sizes were used as reported earlier, the small reactor having a net volume of 23.6 ml. while the larger reactor used for most runs had a net volume of 154.6 ml. The large reactor was coupled to a small outlet cyclone which was also contained in the furnace. Therefore, the cyclone volume (22 ml.) was also available for further reaction. In the residence times reported for the large reactor, this cyclone volume was not included in the residence time calculation, so that residence times reported are reactor gas residence times. A sketch of the larger bench scale reactor is given in Figure 1.

Although most of the experiments carried out were done using the bench scale fluidized bed units, some tests were done in a larger scale unit, originally developed for the pyrolysis of biomass. This unit has been described in other publications (Scott and Piskorz, 1984). A schematic drawing of the pyrolysis unit is shown in Figure 2. The reactor was modified for coal pyrolysis by the addition of three cartridge type heaters immersed in the fluid sand bed, each having a capacity of 500 W watts. Recycle product gas was used as the fluidizing gas, and coal was fed to a pneumatic delivery system by a twin screw feeder. Also, somewhat coarser coal was used in the larger unit which had a feed rate of 1.3 - 1.5 kg/hr.

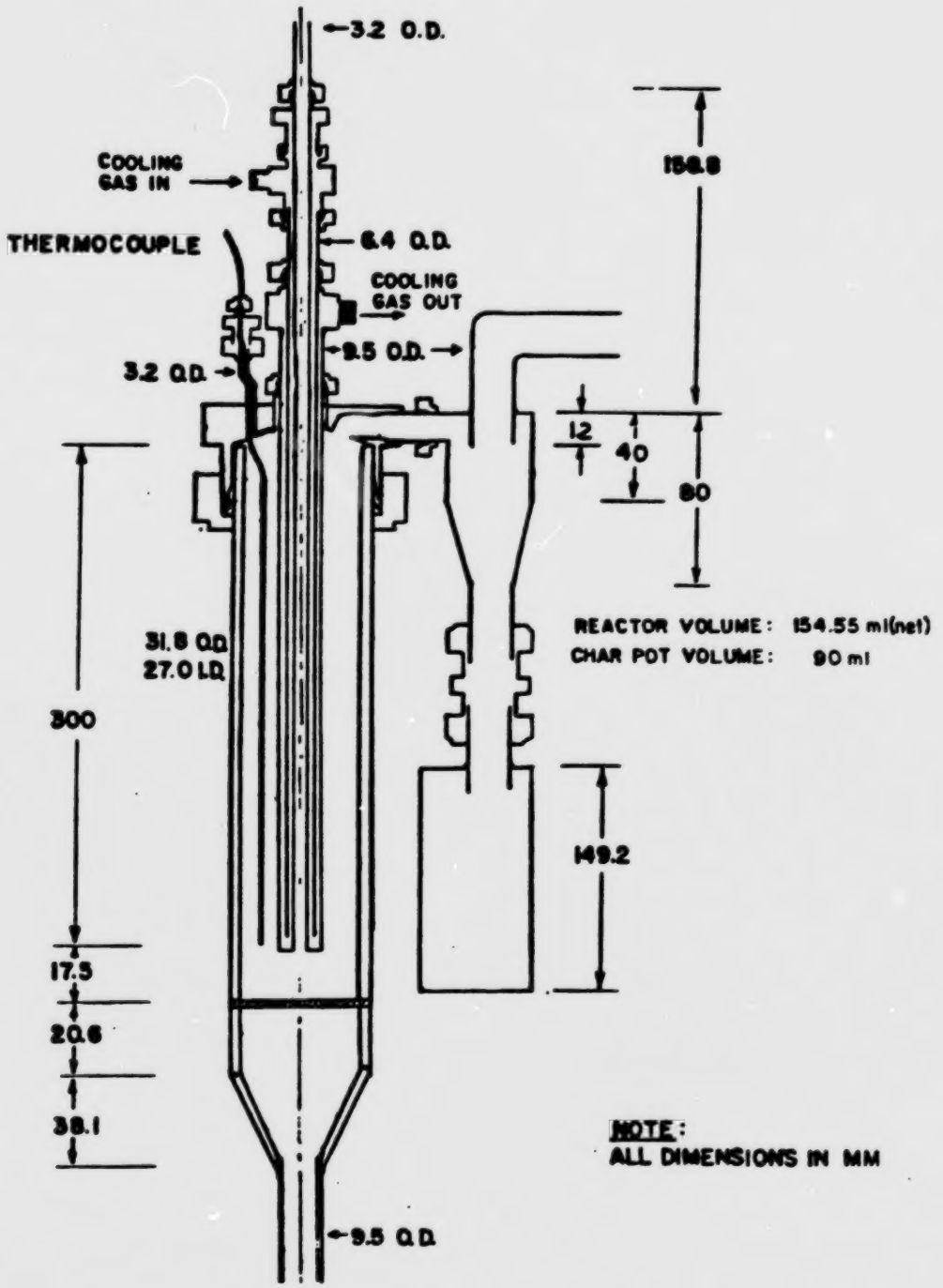

Figure 1 Details of Large Fluid Bed Reactor.

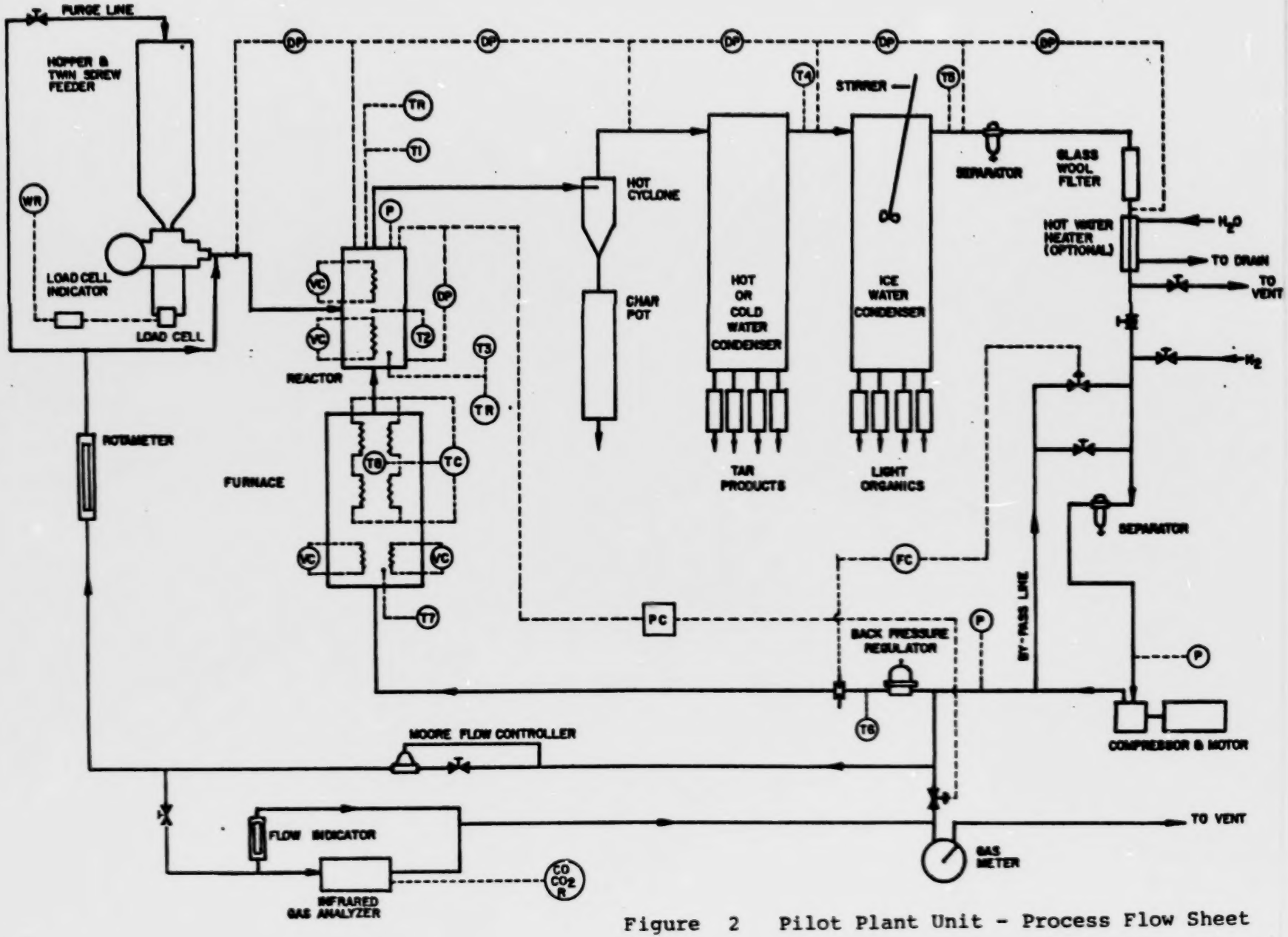

Figure 2 Pilot Plant Unit - Process Flow Sheet

Details of materials used and experimental procedures are given in the following sections.

Coal Preparation and Pretreatment

The coals used in this study include two lignites, three sub-bituminous coals and two bituminous coals as listed below. All samples were supplied by the Energy Research Laboratories of CANMET, Bells Corners, Ontario.

1. Saskatchewan Lignite (Estevan) - a strip mined Saskatchewan lignite. Sample #4 received June, 1984.

2. Saskatchewan Lignite (Coronach) - a strip mined Saskatchewan lignite. Received January, 1985.

3. Forestburg - an Alberta sub-bituminous C coal. Received June, 1984. Sample #2

4. Highvale (Wabamun) - an Alberta sub-bituminous B coal.

5. Hat Creek - a high ash, British Columbia sub-bituminous coal. Received August, 1983.

6. Devco - a high volatile bituminous Nova Scotia caking coal.

7. Balmer - a low volatile bituminous British Columbia caking coal. Received June, 1984. Sample #2

These coals have been ground in a Sturtevant Sample Grinder (Sturtevant Mill Co.) and subsequently size-graded by dry sieving in a Ro-Tap Testing Sieve Shaker (C.E. Tyler Industrial Products). Various particle size fractions were prepared. The standard coal feed size for the bench scale unit was -250 +74 μm (-60 +200 mesh). The pilot plant utilized a broader particle size range typically including everything less than 1680 μm (12 mesh). Lignite and sub-bituminous coal samples prepared for use in the bench scale unit were air dried at room temperature and dried in N_2 at 110°C to reduce the moisture content to below 10 percent. The pilot plant utilized coals as received. Some of the coals have been subjected to further treatments in order to determine the significance of their inorganic fraction.

Coal Characterization

All the coals have been characterized by ultimate and proximate analysis. Estevan lignite and Forestburg sub-bituminous coal samples have also been characterized by petrographic analysis. CHN analysis of the coals was done using a Perkin-Elmer Model 240C Elemental Analyzer. This method required a 1-3 mg sample of coal ground to pass a 200 mesh (74 μm) screen. In addition to the CHN data, the ash content of the sample was also determined. Because of the very small sample size, this ash value may not have been representative of the whole. This sample ash content was used however to calculate the CHN content of the coal on an maf basis. With this data the O content of the coal was calculated by difference. To obtain a

representative ash content three 1 g samples were combusted in air at 950°C for about 2 hours. Similarly, moisture was determined by drying three 1 g samples in air at 110°C for about 24 hours.

Complete proximate analyses of the coals have been done by various sources. All coals have been analyzed using standard ASTM methods. Estevan lignite #4 and Forestburg sub-bituminous coal samples have also been analyzed using microcomputer controlled thermogravimetry (Perkin-Elmer Model TGS-2). This method, described by Earnest and Fyans (1982), provides a rapid determination of moisture, total volatiles, fixed carbon, and ash content of coal which agree with results from the more time consuming standard ASTM methods. Only 5 to 10 mg. of coal are required for the analysis. Because of the small sample size it was decided that moisture and ash contents were best determined from the larger 1 g samples as described above.

Estevan lignite #4 and Forestburg sub-bituminous coal samples have also been characterized by petrographic analysis. The analyses were done by the Energy Research Unit of the University of Saskatchewan, Regina, Saskatchewan. The coals were analysed according to the modified I.C.C.P. maceral classification and reflectance data were obtained on huminite macerals in the coal.

Acid Washing

Several coal samples have been treated in an aqueous acid solution of various strengths to reduce the mineral matter content of the coal. The general procedure consisted of mixing a known weight of coal with enough distilled water to effect a well mixed slurry. The pH of the slurry was recorded and acid was added to lower the pH to the desired value. Additional acid was added as required to hold the pH at this value for 20 minutes while the reaction proceeded. With the reaction complete, the slurry was filtered and the coal was successively washed with distilled water and filtered to remove residual acid. The coal was then dried under N_2 at 110°C. The acid and water wash extracts were combined and stored for cation analysis. One Saskatchewan lignite sample was acid washed three times successively at different acidities. The sample was initially washed as above at a slurry pH of 2.5, filtered, washed and dried and a portion pyrolyzed. The unused portion of the acid washed sample was then further acid treated at a slurry pH of 1.5, filtered, washed and dried and a portion pyrolyzed. The unused portion was again acid treated at a pH of 0.8. The extracts for each acid treatment were saved for cation analysis.

Coal Demineralization

Estevan lignite and Forestburg sub-bituminous coal samples have been demineralized by the method of Bishop and Ward (1958). This procedure entails washing the coal successively with 6N HCl, 29N HF, and 12N HCl for periods of 1 hour at 55° to 60°C.

Carboxyl Group Determination

A portion of the demineralized sample of Estevan lignite was analyzed to determine the carboxyl group content in the raw coal. The method was taken from Morgan, Jenkins and Walker (1981). The H-form carboxyl groups were exchanged with barium acetate releasing one mole of acetic acid for every mole of carboxyl groups exchanged. The solution was titrated with barium hydroxide until the pH was restored to its initial value (8.25-8.30). The quantity of barium hydroxide utilized was used to calculate the number of carboxyl groups exchanged. To check this carboxyl group determination, the amount of barium exchanged onto the coal was determined by back exchanging with perchloric acid. The coal was first washed with sodium acetate to remove any residual barium acetate. The exchanged and washed coal was then boiled in perchloric acid and the solution was analyzed for barium by emission spectrometry. The carboxyl group content was calculated by assuming two carboxyl groups to be exchanged with each barium ion.

Exchangeable Cation Determination

Four different coals have been subjected to ion exchange with ammonium acetate (NH_4Ac) in order to selectively remove only the exchangeable cations and leave essentially intact the discrete mineral matter. The exchanged coals are Saskatchewan lignite #4, Forestburg sub-bituminous, oxidized Forestburg and Hat Creek sub-bituminous. The procedure was adapted from the work of Morgan, Jenkins and Walker (1981). A 1.2N NH_4Ac solution

was prepared and adjusted for a pH of 7.1. One g of raw coal was mixed with 50 ml. of 1.2N NH_4Ac and stirred at room temperature for about 16.5 hours. The coal was then filtered, rinsed with fresh 1.2N solution and subjected again to a 2.5 hour exchange with another 50 ml. of fresh solution, followed by the same washing procedure. Three more exchange cycles were done with successive exchange times of 2.25, 17.75 and 4.25 hours. The total exchange time was about 43 hours. The filtrates were collected after each cycle and analyzed for the exchanged Ca, Mg, Na and K. The results will indicate the progress of the exchange reaction for each cation and also give the total amount of those exchangeable cations present in the raw coal.

Ash Analysis

High temperature ash samples were analyzed for Ca, Mg, Na and K. The results should indicate the total amount of these elements present in the raw coal and thus provide a check for the results obtained from the demineralization procedure and exchangeable cation determination. Na and K contents in the ash, however, may be lower than those in the coal due to partial volatilization of these elements during the ashing procedure. The Ca and Mg in the coal should remain entirely in the ash. About 3 to 5 g of raw coal (-60 +200 mesh) were ashed in air at 950°C. The ash digestion procedure is taken from Perkin-Elmer's A.A. manual. A weighed sample of ash of about 0.1-0.2 g was dissolved in 5 ml. of hot concentrated HF in a 30 ml. nickel crucible. About 4 ml. of $HClO_4$ were added and the solution was

allowed to fume for 2 minutes. A few drops of HCl were added and the solution was cooled slightly. About 20 ml. of 5 percent (v/v) HCl were added and the solution was warmed to obtain complete dissolution. The solution was then diluted to 100 ml. with distilled water and stored for analysis.

Cation Analysis by Atomic Absorption Spectroscopy

The various solutions stored for cation analysis were analyzed by atomic absorption spectroscopy for Ca, Mg, Na and K. The instrument used was a Perkin-Elmer Atomic Absorption Spectrometer Model 303. The samples were diluted so that the concentration of the specific cation being analyzed was within the sensitivity range of the instrument. This meant that sample concentrations had to be 1-10 ppm Ca for Ca analysis, 1-10 ppm K for K analysis, 0.1-2.0 ppm Mg for Mg analysis, and 0.3-3.0 ppm Na for Na analysis. To overcome vapourization and ionization interferences a 5 percent La solution in 25 percent (v/v) HCl was prepared and added to the diluted samples. This resulted in all samples containing one percent La. Corrections were made for cations present in the distilled water and in the La solution.

Bench Scale Pyrolysis

The bench scale pyrolysis unit is shown in Figure 3 and details of the reactor in Figure 3a. The apparatus includes a mechanically stirred entrained flow feeder, a fluidized bed reactor, a cyclone, condensers, filters and gas collection bag. Details of the feeder operation are described elsewhere by Scott and Piskorz (1982). The fluidized bed reactor used during this investigation had a net volume of 154.6 ml. Coal particles were fed to the reactor entrained in a stream of nitrogen. The reactor injection tube could be air cooled to prevent plugging when caking coals were fed. The bed consisted of Ottawa Testing Sand typically screened to -590 +300 μm (-30 +50 mesh). A second stream of nitrogen provided the fluidizing gas for the bed. Vapour residence times could be varied by adjusting the volume of sand in the bed and/or the fluidizing plus feeder gas rate. Following Run 142 a cyclone and char pot were added to separate char and vapour products. The reactor-cyclone-char pot assembly was inside the furnace permitting the pyrolysis reaction and product separation to occur at the same temperature. This prevented the hot vapours from condensing in the char pot. Gas and tar vapours were collected in a split stream system consisting of four ice-water glass condensers, two cotton wool filters and a polyethylene gas bag. Condensible liquid products either condensed on the walls of the glass condensers or formed a fog that was removed by the cotton wool filters. The remaining gaseous product was collected in a sealed polyethylene bag with an approximate volume of 170 L. The total volume of gas collected during a run was measured prior to

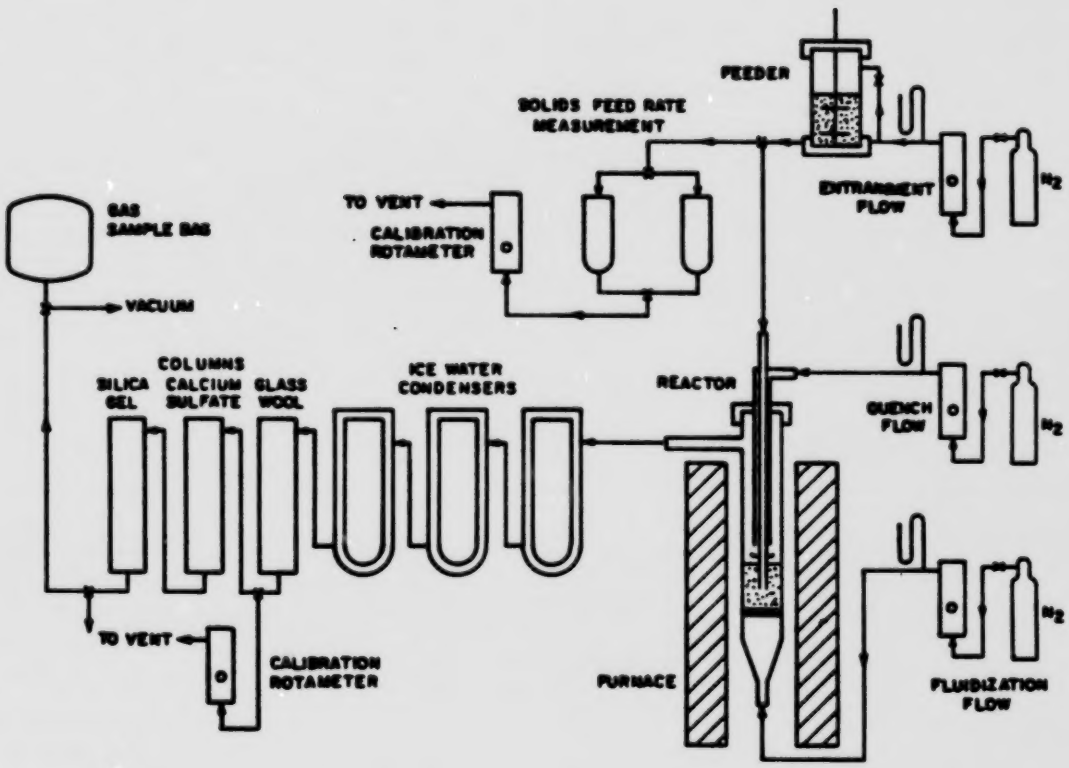

Figure 3 Bench Scale Pyrolysis Unit

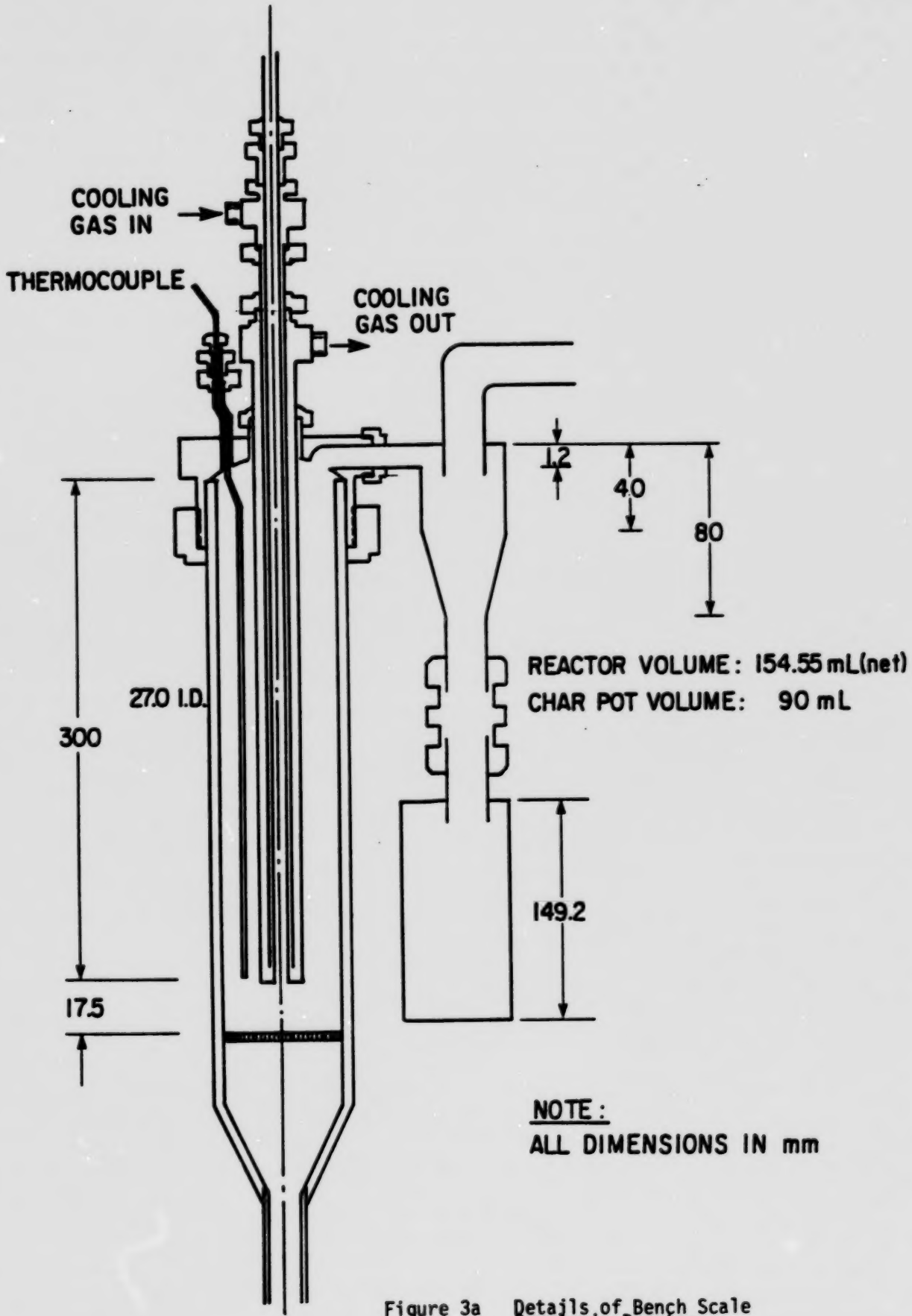

Figure 3a Details of Bench Scale Pyrolysis Reactor

Run 176 by recording the inert gas flow rates and the time of running and adding the volume of product gas calculated using the G.C. analysis. After Run 176 a dry gas meter measured the total volume of gases collected. The absorption tubes for water and light hydrocarbons were optional and were not normally used in coal pyrolysis studies.

A smaller version of the original Scott feeder was constructed which has a smaller dead volume below the entrainment tube. This allows the pyrolysis of smaller samples of coal. The large feeder required more than 100 g of coal before it could begin to operate whereas the small feeder is capable of feeding all but about 15 g of the feed charge.

Product Collection and Analysis

Analysis of the gas sample for CO, CO_2, H_2, C_1 to C_4 hydrocarbons, BTX and water was performed using two gas chromatographs. The instruments and procedures for this analysis are summarized in Table 1. The product gas composition was calculated on an N_2-free basis. Knowing the volume and composition of the gas collected, the percent conversion of the coal to gaseous components can be calculated.

Two 15 ml. sample vials connected beneath the first two condensers were used to collect water and water soluble oils. The water content of this liquor was determined by Karl-Fischer titration. The quantity of tar stopped by the cotton wool filters was determined by weighing the filters before and after

Table 1

Instruments and Procedures for Gas Product Analysis

data station : Perkin-Elmer Sigma 10B

instrument A : Perkin-Elmer Sigma 4B gas chromatograph

detector	thermal conductivity
carrier gas	helium
gas flow rate(ml/min)	25
inlet pressure(psi)	20

Column A : Molecular Sieve 5A

compounds analysed	hydrogen,carbon monoxide
size	6'x0.125" OD (80/100 mesh)
temperature(C)	60

Column B : Poropak Q

compounds analysed	carbon dioxide,water
size	8'x0.125" OD (80/100 mesh)
temperature(C)	60

instrument B : Perkin-Elmer Sigma 3B gas chromatograph

detector	flame ionization
carrier gas	nitrogen
gas flow rate(ml/min)	30
inlet pressure (psi)	80

Column A : 10% Flourad FC-431 on WHP

compounds analysed	benzene,toluene,xylene
size	6'x0.125" OD (80/100)
temperature(C)	45 for 4 min 8 deg/min increase 195 for 10 min

Column B : Poropak Q

compounds analysed	methane,ethanes,propanes,butanes
size	6'x0.125" OD (80/100 mesh)
temperature	45 for 4 min 8 deg/min increase 195 for 10 min

the run. The remaining tar was washed from the condenser walls and tubing with a mixed solvent of methanol/methylene chloride. The washings were filtered to remove any char and the water content of the solution was determined by Karl-Fischer titration. The solvent was then evaporated at 66°C under 20" Hg vacuum. The tar residue was weighed and dissolved in about 15 ml. of tetrahydrofuran (THF) and the water content was again measured to determine the amount of water remaining in the residue after solvent evaporation.

The reactor-cyclone-char pot assembly was weighed before and after each run to determine the quantity of char collected in the char pot and in the bed. Typically very little char accumulation in the bed occurred. The char filtered from the solvent washings was dried and weighed and included in the char determination.

Material balances were calculated knowing the weight of coal fed and the quantities of char, tar, water and gas collected. Ultimate analyses of the char and tar products were done. Combining these data with the coal feed ultimate analysis and gas analysis allows the calculation of elemental balances for C, H, N and O for each run. Using the char ash content determined by the elemental analyzer, ash balances are also calculated.

Pyrolysis in a CO_2 Atmosphere

Procedures for the pyrolysis of coal in a CO_2 atmosphere are very similar to those for a nitrogen atmosphere. Prior to the run CO_2 was bubbled through the coal in the feeder and passed through the cotton wool filters to displace all the air from the

system. Thus, the coal feed and cotton wool were saturated with CO_2 both before and after the run when their weights were recorded. Following the run it was impossible to distinguish between CO_2 added to the system and pyrolytic CO_2 produced during the run. For this reason CO_2 was not determined in the gas product. Other procedures are identical to those for pyrolysis in N_2.

Pyrolysis in a Steam Atmosphere

Several pyrolysis runs have been done in a steam-N_2 atmosphere. Coal was fed into the reactor entrained in a stream of N_2. Steam was used to fluidize the sand in the bed. The steam partial pressure in the reactor ranged from 0.61 atm. at 550°C to 0.69 atm. at 650°C. Steam was generated by pumping about 2.5 ml./min. of water from a polyethylene bottle through about 2' of coiled 1/16" S.S. tubing running through the furnace. An FMI Lab Pump (Model RP-G6) was used to pump the water and an FMI Pulse Dampener (#PD-60-LF) reduced the fluctuations in water flow. During the run the steam was completely condensed in the first set of condensers while the tar vapours collected in both the condensers and the cotton wool filters. Since much of the system gaswas condensed, the gases collected were relatively concentrated in pyrolysis products. Other procedures were identical to those for N_2 pyrolysis.

Pilot Plant Pyrolysis

Several runs have been made on the 2 kg/hr pilot plant unit to confirm pyrolysis results obtained from the bench scale unit. The process flow sheet for the pilot plant was shown previously as Figure 2. Coal was charged to a hopper with a twin screw feeder and conveyed pneumatically to the fluidized bed reactor. An electrical furnace surrounding the gas inlet line and the plenum chamber supplied most of the heat to the bed of sand. Additional heat was supplied by three electrical cartridge heaters immersed in the bed. During a run char was separated from the volatile products by an insulated cyclone and collected in a cold char pot. The volatile products then passed through a system of two condensers, two separators, and a cotton wool filter connected in series. The temperature in the first condenser was maintained by either hot or cold water and could be controlled over the range of about 15°to 60°C. The temperature of the second condenser was maintained by ice water and usually approached 0°C. Four plastic sample bottles were connected beneath each condenser to collect any flowing condensed liquid products. A Schrader bellows pot was connected after each condenser and helped to separate any entrained liquid or solid from the gas stream. Finally a cotton wool filter stopped the remaining tar fog and allowed a fairly clean product gas. A constant system pressure was maintained by venting the volume of pyrolysis gas produced through a gas meter and then through a pressure control valve. An Anarad Infrared Gas Analyzer Series AR-400 gave a continuous reading of CO and CO_2 gas percentages in

the product gas. A gas compressor maintained the circulation of gases required to fluidize the bed of sand and to convey coal from the feeder. As a run progressed the pyrolysis gas constituted an increasing percentage of the total system gas as it replaced the original nitrogen gas in the system.

Product Collection and Analysis

Approximately 1 L of pyrolysis gas was collected in a sealed polyethylene bag at any time during a run. Analysis of the sample was the same as for the bench scale unit. Although the gas concentration of pyrolysis products was increasing during a run, the gas composition expressed on an N_2-free basis was constant. Since the gas meter provided the volume of pyrolysis gas produced, the percent conversion to gaseous products could be calculated.

Liquid product collection from the pilot plant was similar to that from the bench scale unit. Eight 1 L plastic bottles collected mostly water and water soluble products from the two condensers. The water content of this fraction was determined by Karl-Fischer titration. The cotton wool filter was weighed to determine the quantity of tar collected and the cotton wool was discarded. Products collected in the Schrader bellows separators were weighed and stored. The remaining tar was washed from the condenser piping with a mixed solvent of THF/methanol/methylene chloride. The wash solution was filtered to remove char and its water content determined by Karl-Fischer titration. The solvent was then evaporated at 66°C and 20" Hg vacuum and the tar residue was weighed and stored.

Char production was determined from the weight of char in the char pot and from the quantity of char filtered from the solvent washings. Char was removed from the char pot and stored for analysis. Knowing the weight of coal fed and the quantities of char, tar, water and gas produced, material balances were calculated.

Ultimate analyses of the char and tar products were performed using the Perkin-Elmer Model 240 Elemental Analyzer. As with coal, char ash content was determined by combusting two or three 1 g char samples in air at 950°C for about 2 hours. These data combined with the gas analysis and coal feed ultimate analysis allowed the calculation of elemental balances for C, H, N and O as well as an ash balance for a run.

Char Characterization by Thermogravimetric Analysis

Char products produced from several raw and acid washed coals have been characterized by thermogravimetric analysis in nitrogen and carbon dioxide. The instrument used was a Perkin-Elmer Model TGS-2 Thermobalance. Chars were produced in the thermobalance by drying each coal in N_2 for 5 min. at 110°C followed by increasing the temperature at 100°C/min. to a maximum of 950°C. After complete devolatilization, CO_2 was introduced at a constant temperature of 950°C, and the weight loss-time history recorded. This final weight loss was due only to the char-CO_2 reaction and thus the char reactivities could be calculated.

Char reactivities were determined as functions of coal rank and type of pretreatment.

Petrographic Analysis

Various chars produced from the bench scale pyrolysis of raw Forestburg sub-bituminous and raw and acid washed Estevan lignite were characterized by petrographic analysis. The Energy Research Unit at the University of Saskatchewan performed the analysis. The char components were divided into unaltered coal, isotropic and anisotropic coal and mineral matter. The chars were also characterized according to their vesicular or non-vesicular appearance and by their reflectance of huminite products.

MATERIALS USED

The analyses of the various coals used, both proximate and ultimate analyses, were carried out both by standard methods of analysis, and were checked by other methods as well. Some of the coals used were fresh batches, and are designated as Saskatchewan (Estevan) lignite No. 4, Forestburg No. 2, etc., to distinguish them from previous samples from the same deposits. As well as our own analyses, comparisons were made to analyses by others of samples (not the same as our sample) from the same deposits.

Table 2 and Table 3 give ultimate and proximate analyses of our older samples of Balmer bituminous and Forestburg sub-bituminous coal, as well as the analyses for a 50/50 weight percent mixture of the two coals. This mixture was used in tests investigating methods of controlling coal agglomeration during pyrolysis in a fluidized bed. In addition, analyses of similar coals given by Furimsky (1981), by Al-Jarallah (1983) and by the Alberta Research Council (Du Plessis, 1982) are given for comparison. The results illustrate the difficulty in obtaining comparison of results among various workers because of the variability in the composition of the coal samples used.

Tables 4 and 5 give ultimate and proximate analyses of the fresh samples of Balmer bituminous #2, Forestburg sub-bituminous #2 and Saskatchewan (Estevan) lignite #4. Proximate analysis was carried out by TGA techniques, and both N_2 and CO_2 were used as sweep gases. A typical TGA determination for the Saskatchewan lignite #4 proximate analysis is shown in Figure 4. The use of

Table 2

Properties of Balmer and Forestburg Coals
and of Balmer-Forestburg Mixture (50:50 by weight)

Ultimate Analysis, wt.% M.A.F. basis

		C	H	S	N	O (by diff.)
Waterloo	(REMS) Balmer	89.42	4.61	ND	1.50	4.46
	Forestburg	68.93	4.36	ND	1.45	25.26
	Forest-Balmer	80.56	4.35	ND	1.63	13.46
Furimsky	(1) Balmer	90.1	4.9	0.2	1.7	3.0
U.B.C.	(2) Balmer B	89.38	4.8	0.25	1.14	4.43
	Forestburg	76.4	4.02	0.58	1.71	17.3
A.R.C.	(3) Forestburg (Vesta 1)	74.5	4.2	0.6	1.8	18.9
	Forestburg (Vesta 2)	72.0	4.4	0.6	1.7	21.3

Table 3

Proximate Analysis, wt.% as is basis

		Moisture	Volatiles	Fixed Carbon	Ash
Waterloo	Balmer	0.8	ND	ND	8.8
	Forestburg	10.02	40.95	41.55	7.48
	Balmer-Forestburg	3.06	ND	ND	8.33(8.59 MF)
Furimsky	Balmer	0.7	20.2	68.8	10.3
U.B.C.	Balmer B	1.47	20.07	66.95	11.51
	Forestburg	23.17	32.96 (42.90 MF)	37.18 (48.39 MF)	6.69 (8.71 MF)
A.R.C.	Forestburg (Vesta 1)	0	37.1	50.0	12.9 } Moisture
	Forestburg (Vesta 2)	0	38.4	50.9	10.7 Free

Properties of Balmer, Forestburg, and Saskatchewan Lignite Coal Samples

Table 4

Ultimate Analysis, wt. % MAF basis

	C	H	N	O (by diff.)
Balmer bituminous Sample #2, -60 mesh	87.50	4.39	1.27	6.84
Forestburg sub-bituminous Sample #2, -60 mesh	69.85	3.65	1.88	24.62
Saskatchewan lignite Sample #4, -60 +230 mesh	67.58	4.26	1.17	26.99

Table 5

Proximate Analysis, wt. % 'as is' basis

		Moisture	Volatiles	Fixed Carbon	Ash
Balmer #2	TGA in N_2	0.43	22.49	65.76	11.39
	TGA in CO_2	0.61	22.06	65.66	10.99
	Furnace	0.68			11.40
	Elemental Analyzer				11.22
Forestburg #2	TGA in N_2	11.36	38.33	44.73	5.41
	Furnace	11.06			5.62
	Elemental Analyzer				5.80
Saskatchewan	TGA in N_2	6.66	41.66	45.42	6.24
Lignite #4	TGA in CO_2	2.93	93.85		3.22
	Furnace	6.68			6.25
	Elemental Analyzer				6.04

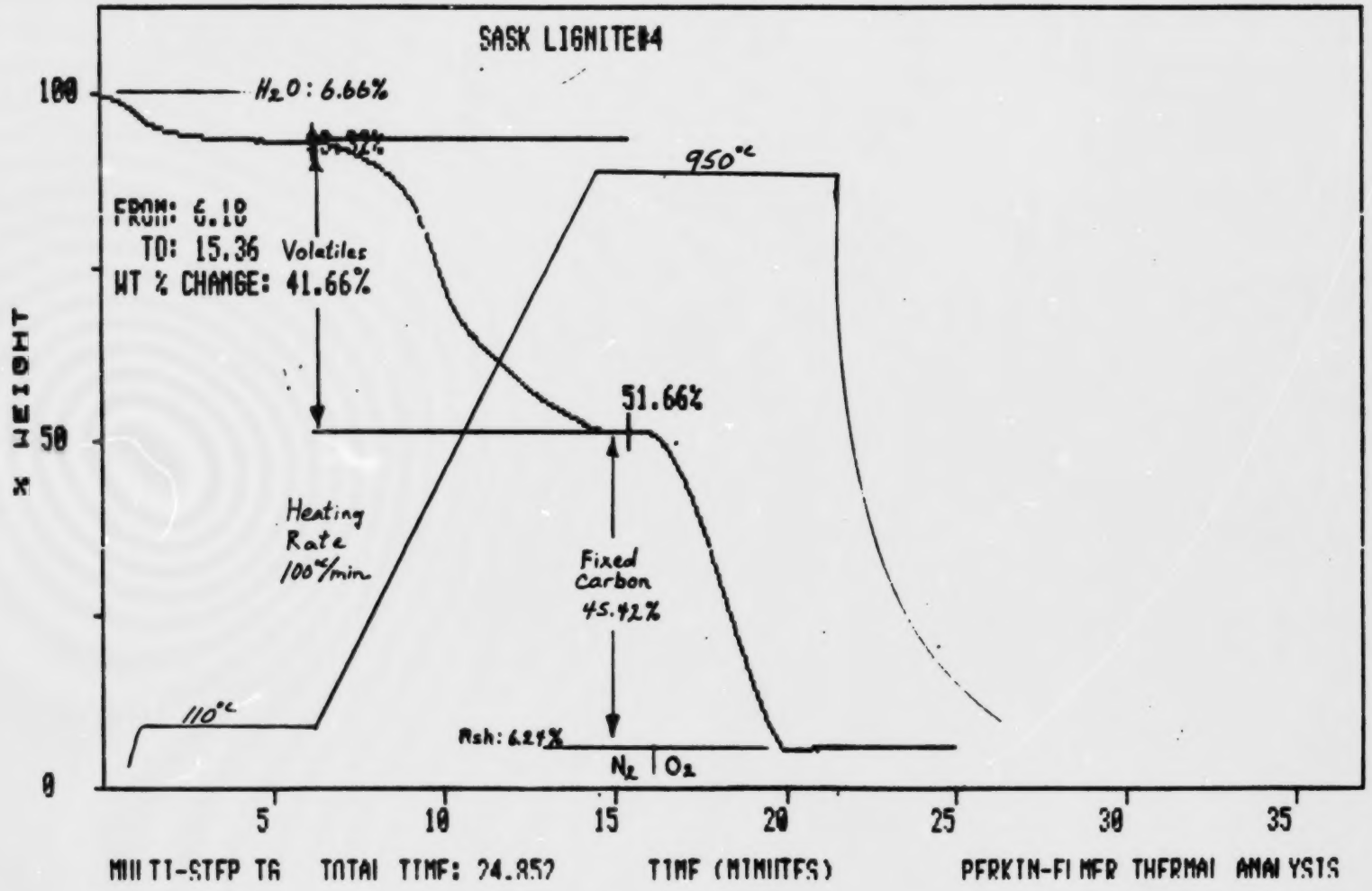

Figure 4 Thermogram of Saskatchewan Lignite Coal Sample #4 in N_2

CO_2 in place of N_2 gives very similar results with a refractory coal such as the low volatile high rank Balmer bituminous coal. However, the reactivity of the carbon in the low rank lignite is apparent when CO_2 is used as the gaseous atmosphere during the proximate analysis. Hence, only the values in N_2 should be used as proximate analysis results. However, the differences apparent in the reactivities of coals to CO_2 during this procedure led to an adaptation of the method to give a means of measuring char reactivities for different coals.

Although ash contents given in Table 5 from the furnace ashing method and from the TGA method agree well, the values from the furnace method were used as the more accurate when available. As explained previously, TGA ash determinations have a large inherent error due to the very small sample size used.

Tables 6A and 6B give proximate and ultimate analyses for the coals used in our earlier work, and are taken from that final contract report (Scott, 1984). All the coals used in this work except for the Estevan lignite, the Forestburg and the Balmer coals were the same samples as those whose analyses are reported in Tables 6A and 6B.

Proximate and ultimate analyses were also performed on acid extracted coals used as pyrolysis feeds. These analyses are given in the "Results" section.

Table 6A

Proximate Analyses

Type	Ash %	Moisture %	FC %	VM %	FC maf %	VM maf %	Oil Yield Fischer maf % (3)	FSI %
Estevan Lignite I (2)	8.25	28.4	34.75	28.61	54.85	45.15	-	0
Estevan Lignite 3 (1)	6.29	7.93	42.67	43.11	49.74	50.26	-	
Forestburg (1)	6.5	10.0	41.96	41.31	50.25	49.47	-	0
Highvale (1)	10.7	17.3	44.50	29.17	61.80	40.51	5.9	0
Hat Creek (1)	50.7	4.0	14.8	30.5	32.67	67.33	-	0
MacIntyre (2)	7.47	0.79	74.24	17.50	80.92	19.08	3.7	4.5
Balmer (2)	9.78	0.64	69.71	19.87	77.82	22.18	6.4	4.0
Sukunka (1)	9.00	1.88	69.9	21.1	78.4	23.7	5.2	3.7
Devco (1)	2.9	1.2	60.96	34.98	63.56	36.47	14.2	8.5

(1) Analysis by Coal Research Laboratory, University of Waterloo.

(2) Analysis by Energy Research Laboratories, CANMET.

(3) Furimsky et al (1981)

Table 6B

Ultimate Analyses

maf basis

Type	C %	H%	S%	N%	O % (by difference)	H/C
Sask. Lignite I (2)	70.82	4.75	0.64	1.28	22.51	.80
Sask. Lignite 3 (1)	71.2	4.24	N.D.	1.64	22.9	.71
Forestburg (1)	71.2	4.50	0.60	1.53	22.2	.76
Highvale (1)	75.4	4.1	0.2	1.10	19.3	.65
Hat Creek (1)	60.36	2.8	N.D.	1.54	32.7	.56
MacIntyre (2)	93.13	4.66	0.46	1.30	0.46	.60
(1)	88.68	4.4	N.D.	1.2	5.7	.60
Balmer (2)	90.36	4.79	0.30	1.26	3.29	.64
(1)	89.08	4.28	N.D.	1.45	5.19	.58
Sukunka (2)	86.2	4.53	0.69	1.75	3.1	.63
Devco (2)	87.14	5.50	1.09	1.73	4.54	.76
(1)	86.33	5.48	N.D.	1.82	5.28	.76

(1) Analyses by Coal Research Laboratory, University of Waterloo.
(2) Analyses by Energy Research Laboratories, CANMET.

RESULTS AND DISCUSSION

(i) Acid Washing of Estevan (Saskatchewan) Lignite

(a) Cation Analysis of Raw Coal

Preliminary tests reported previously (Scott, 1984) had shown that a significant increase in tar yield could be achieved from a Saskatchewan lignite by prior acid washing. Presumably this treatment removes metallic cations which act as gasification promoters (Tyler, 1980; Morgan et al., 1981), and because of the fact that they can be displaced by hydrogen ions, they are assumed to be associated with the organic matter of the coal. However, the same cations may also be incorporated into the mineral matter of the raw coal, and because of this factor, analyses of specific cations must be carefully done.

In the present tests, several methods of analysis were attempted to measure the total amounts of specific cations in the coal (that is, the combined amount in the mineral matter and in the organic matrix). These analytical values need to be accurately known to allow calculations to be carried out so that it can be determined what fraction of a cation may be in the exchangeable form.

The first method used was the total demineralizing method of Bishop and Ward (1958). This demineralization procedure entails washing the coal successively with 6N HCl, 29N HF and 12 N HCl for periods of one hour at 55°-60°C. Using this procedure a 10 gram sample of Estevan lignite #4 was completely

demineralized, as shown by a 0.0% ash content. The extract solutions were then analyzed by plasma emission spectroscopy for Al, Fe, Ca, Mg, K and Na. The acid extract was also analyzed for carbon, and about 0.1% of the coal carbon was found to have been also removed, indicating that very little organic matter is simultaneously extracted.

A second method of total cation analysis followed the procedure suggested by Perkin-Elmer for ash digestion (Perkin-Elmer Co, 1979), with analysis of the extract solution. The procedure is intended primarily for the analysis of total calcium in coal, and involves digestion of ash (950 C) in warm hydrofluoric and perchloric acid, followed by treatment with cold concentrated HCl.

A third method was intended to measure the amount of exchangeable cations associated with organic matter in the coal, and utilized ion exchange between the coal and ammonium acetate, with subsequent analysis of the spent ammonium acetate solution (Morgan et al., 1981).

None of the three methods appeared to give completely satisfactory results for all cations. For example, the ash digestion method gave generally higher mineral matter values than did the total demineralizing procedure. On the other hand, the ion exchange technique gave higher sodium values than either of the other two methods. In the case of the ash digestion method, this result is probably due to the partial loss of volatile sodium from the ash at the high ashing temperature of 950°C, as

suggested by Berkowitz (1979). In the end, and after repeated duplicate analyses, the true mineral matter contents of the raw coals were assumed to be the highest values obtained for each cation by either the ash digestion analysis or the exchangeable cation determination. Early analyses of the cation content of extract solutions had to be discarded due to a small residual cation content of the ion exchanged water used for the final dilution before analysis. In the results reported here, a pure water with negligible cation content (<0.1 ppm) was used for all spectroscopic measurements.

A summary of the results for the raw coal is given in Table 7. For comparison, an ash analysis reported by Van der Heijden and Barua (1980) is also shown. For the four cations reported in Table 7, the values based on the dry coal are in better agreement with our results than the values reported as a percent of the ash. If the four cations are associated largely with the organic matter of the coal rather than the mineral matter, then this agreement would be expected. The amounts of exchangeable Ca, Mg, Na and K measured agree also with the amounts in the ash expressed as a percent of the coal weight, confirming that nearly all of these cations were associated with the organic phase of the coal.

(b) **Acid Washing Tests**

Tests were done to assess the effects of acid washing on tar yields from Estevan Lignite coal sample #4. Four levels of acid washing were performed and each acid washed sample was

Table 7

Chemical Analysis of Ash in Coal
Estevan Lignite #4

(1) weight percent dry coal from ash analysis
(2) weight percent of ash
(3) exchangeable cations, weight percent dry coal
(4) cations by exchange/cations by ash analysis X 100

	Sask. Power*		U. of W.**		U. of W.**	
	(1)	(2)	(1)	(2)	(3)	(4)
Ca	1.14	7.14	1.05	10.99	1.07	102
Mg	0.26	1.62	0.23	2.41	0.25	109
Na	0.59	3.74	0.65	6.81	1.21	186
K	0.12	0.74	0.04	0.42	0.06	156
Total	2.11	13.24	1.97	20.63	2.59	
Ash, dry wt.%	15.9 (750°C)		9.55 (950°C)			

* Van der Heijden, S., Barau, S.K., "Lignite Reactivity - II Final Report" May 1980

** Analysis by A. Royce, University of Waterloo

pyrolyzed under similar conditions. It was expected that acid washing would remove the exchangeable alkali cations from the coal which are thought to adversely affect tar and oil yields. Certain cations should be selectively removed at the different strengths of acid used. Cation analysis of the original coal and of the aqueous wash extract was done to determine the degree of removal of each cation, and to provide insight into the effect of specific cations on the tar and oil yields.

A sample of 500 grams of Estevan Lignite #4 screened to -250 µm +63 µm (-60 +230 mesh) was slurried with distilled water and sufficient 6N HCl added to bring the pH to 2.5. Additional acid was added as required to hold the pH at 2.5 for 20 minutes while the reaction proceeded. With the reaction complete, the slurry was filtered and the coal was successively washed with distilled water and filtered to remove residual acid. The coal was dried under N at 110°C and a quantity was then pyrolyzed (Run 161) in the bench scale unit. The unused portion of the acid-washed sample was further acid treated at a slurry pH of 1.5, filtered, washed and dried, and a portion pyrolyzed (Run 162). The unused fraction was acid treated again at a slurry pH of 0.8 and a portion pyrolyzed in N_2 (Run 163) and a second portion was pyrolyzed in a CO_2 atmosphere (Run 164). A fresh 220 gram sample was acid washed as described above at a pH of 3.5 and after washing and drying was pyrolyzed with N_2 (Run 165). Each washing extract was saved for cation analysis.

Subsequent results from pyrolysis tests suggest that the degree of cation removal may be affected both by solution equilibrium and to a lesser degree by the particle size distribution. If the solid ion-exchange functionalities of the coal come to equilibrium with the extracting solution, then the method of carrying out the extraction may have some effect on the degree of cation removal. For example, a single stage extraction to a pH of 1.5 would not give quite as good results as a two step extraction to the same final pH level with intermediate filtration and washing of the coal.

Another sample was acid washed following the above procedures to a pH of only 4.0, which was the lowest level of acid washing used. Two pyrolysis runs were done with this extracted coal sample (Runs 166 and 167) at 650°C and 550°C respectively, and using the same pyrolysis conditions as for the other acid washed samples.

Mineral matter contents of acid washed Saskatchewan lignite samples are shown in Table 8. The mineral contents in the acid wash extracts were determined and these quantities were subtracted from the mineral content of the raw coal to obtain the values for the acid washed coal samples. From the results shown in Table 8, it is apparent that the coal mineral cation contents decrease with increasing severity of acid treatment. Figure 5 shows the variation of cation content with the pH of the wash solution. Over 90 percent of the calcium and magnesium but only 64 percent of the sodium were removed at the lowest acid wash pH of 0.8. The sodium appears to be removed in a stepwise fashion

Table 8

Mineral Matter Content of Acid Washed Coal

Estevan Lignite #4 -60 +230 mesh

(1) weight percent dry coal
(2) gram equivalents per kg dry coal

	Raw by NH_4Ac Ex.		pH = 4.0 HCl		pH = 3.5 HCl		pH = 3.0 H_2SO_3		pH = 3.0 H_2SO_4		pH = 2.5 HCl		pH = 1.5 HCl		pH = 0.8 HCl	
	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)
Ca	1.07	0.53	0.94	0.47	0.80	0.40	0.80	0.40	0.75	0.37	0.33	0.16	0.15	0.07	0.09	0.04
Mg	0.25	0.21	0.19	0.16	0.14	0.12	0.12	0.10	0.07	0.06	0.04	0.03	0.03	0.02	0.02	0.02
Na	1.21	0.53	0.69	0.30	0.65	0.28	0.67	0.29	0.43	0.19	0.47	0.20	0.43	0.19	0.43	0.19
K	0.06	0.02	0.05	0.01	0.05	0.01	0.05	0.01	0.05	0.01	0.05	0.01	0.04	0.01	0.01	0.003
Total	2.59	1.29	1.87	0.94	1.64	0.81	1.64	0.80	1.30	0.63	0.89	0.40	0.65	0.29	0.55	0.25

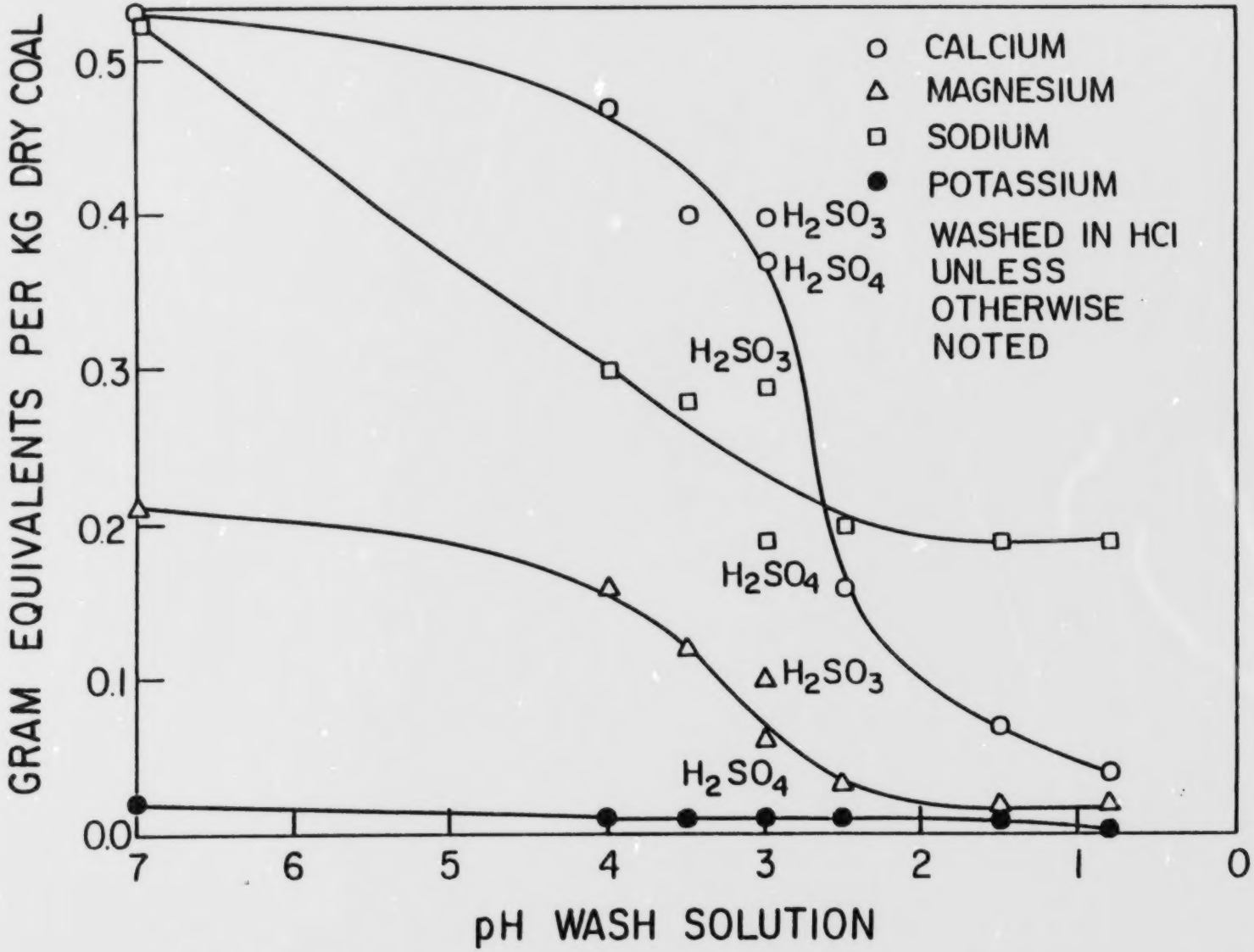

Figure 5 Cation Content vs. pH of Acid Washing for Estevan Lignite #4

as the pH is lowered, suggesting the possibility that two different types of sodium ion are present in the raw coal. One type may be liberated by a relatively weak acid solution (i.e. pH = 4) while the other requires a stronger treatment (i.e. pH = 2). The cation contents given for the lignite samples in Table 8 and Figure 4 which were washed with HCl at pH values of 2.5, 1.5 and 0.8 are actually those of one lignite sample washed three times in succession as described previously. Therefore, if the degree of cation exchange of the coal is equilibrium controlled then the successive washing of a sample will remove a greater portion of the mineral matter than a single wash to the same final pH value.

This hypothesis is supported by the results in Table 9 showing the mineral matter contents of three Saskatchewan lignite samples each washed once only. Very little additional magnesium, potassium or sodium is removed as the wash solution pH is reduced to 0.8 from 2.5. This is also true for the sample washed three times in succession. Additional calcium, however, is removed as the wash solution pH is decreased to 0.8 from 2.5 and this is true for both the singly washed sample and the successively washed sample. Significantly, for the sample washed once at a pH of 0.8, about 25 percent of the original calcium remains in the coal compared to only about 8 percent for the sample washed three times in succession. Therefore it is concluded that successive washes are able to remove more calcium cations than single washes under similar conditions. It is also apparent from the data given in Tables 8 and 9 that 80% of the Mg and about 50% of the Na and K are easily removed at pH $>$ 2.5,

Table 9

Mineral Matter Content of Acid Washed Coal*

Estevan Lignite #4 -200 +230 mesh

(1) weight percent dry coal
(2) gram equivalents per kg dry coal

	Raw by NH_4Ac Ex.		pH = 4.0 HCl		pH = 2.5 HCl		pH = 0.8 HCl	
	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)
Ca	1.07	0.53	0.85	0.42	0.46	0.23	0.27	0.13
Mg	0.25	0.21	0.15	0.12	0.06	0.05	0.04	0.03
Na	1.21	0.53	0.60	0.26	0.55	0.24	0.61	0.27
K	0.06	0.02	0	0	0.05	0.01	0.05	0.01
Total	2.59	1.29	1.60	0.80	1.12	0.53	0.97	0.44

* Single step extractions

whereas stronger acid washes result in very little extra extraction of these cations. The particle size used for the results shown in Table 9 was also somewhat smaller than that corresponding to the test results given in Table 8. However, comparison of the degree of cation removal achieved at the same pH level with single step extraction, for example, at pH values of 4.0 and 2.5, shows only minor differences, and no clear trend. Therefore, within the size range used, and for the extraction conditions used, the particle size did not appear to be a significant variable.

It is a reasonable assumption that the acid consumed during extraction should be a measure of the extent of exchange between the acid and the coal. Figure 6 verifies this assumption by showing the relation between acid consumption, as measured experimentally, and cations removed from the coal. For each calculated gram equivalent of acid consumed approximately 0.85 gram equivalents of calcium, sodium, magnesium and potassium were removed from the coal. The remaining 15 percent of the acid was probably consumed by other inorganic elements which were not determined. These undetermined inorganic elements may consume an increasingly large portion of the acid as the pH of the wash solution drops below 1. This would explain why the curve in Figure 6 flattens out at a pH of 1.5. However, for less acidic solutions (pH $>$ 1.5) acid consumption appears to be a good measure of the extent of exchange of these four elements.

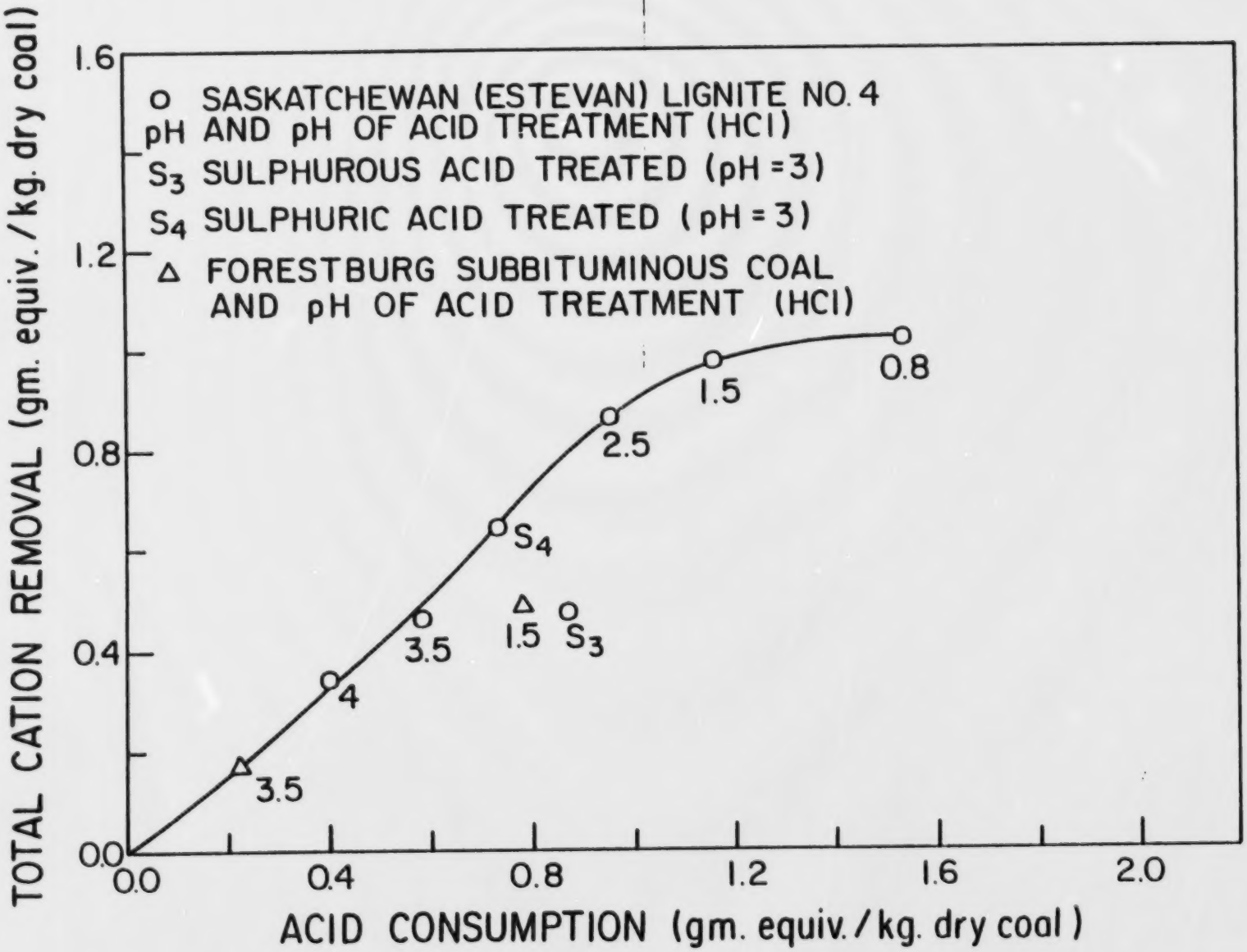

Figure 6 Cation Removal vs. Acid Consumption for Estevan Lignite #4

Aluminum and iron were also determined in the lignite ash and were found to be 1.07% and 0.50% of the coal weight, respectively. Acid extraction at all pH levels removed only small amounts of these elements (about 5%). Ammonium acetate exchange showed negligible amounts of cation exchangeable Al or Fe. Therefore, it was concluded that no Al or Fe was associated with the organic matter of the coal.

(c) Pyrolysis of Acid Washed Lignite

The experimental procedure consisted of pyrolysis using the large reactor with heated cyclone and char pot. Vapour product collection consisted of two parallel streams each with two ice water glass condensers and a cotton wool filter. Gas content determination was by gas chromatography. Liquids were washed out of the condensers using a solvent consisting of about 50 percent dichloromethane and 50 percent methanol. The solvent was evaporated at about 67°C and 20" Hg vacuum, and the liquid product was then weighed, dissolved in tetrahydrofuran, and stored.

Table 10 gives results of pyrolysis runs with the acid washed coal (Runs 161 to 167) as well as Run 160 with untreated coal. The major effect of the acid washing is the increase in tar yield with a parallel reduction of gas yield. The tar yield for Run 165 is nearly 50 percent greater than that for Run 160. The trend, as shown in Figure 7, is to higher tar yields with stronger acid washing. Table 10 also shows the trend to lower gas yields with stronger acid washing. A lower CO_2 yield

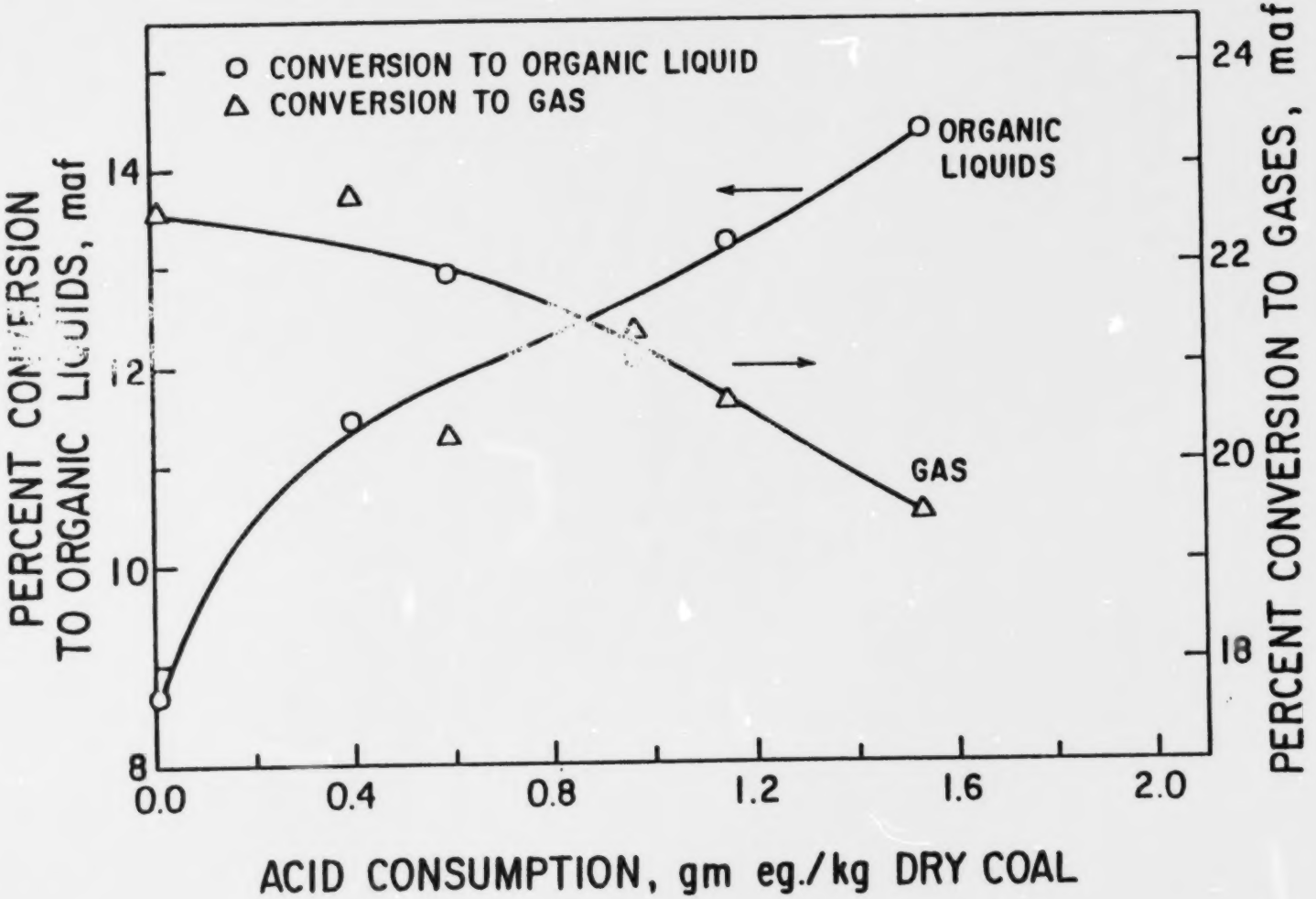

Figure 7 Tar and Gas Yields vs. Acid Consumption for Estevan Lignite #4, 650°C, N_2, 0.55 s.

Table 10

Pyrolysis of Acid Washed Estevan Lignite Coal #4 (July 1984)

Run No.	160	166	167	165	161	162	163	164*
Wash Slurry pH	Not washed	4.0	4.0	3.5	2.5	1.5	0.8	0.8
Temperature, °C	650	650	550	650	650	650	650	650
Coal Size, µm	-210+62	-210+62	-210+62	-210+62	-210+62	-210+62	-210+62	-210+62
Sand Size, µm	-590+300	-590+300	-590+300	-590+300	-590+300	-590+300	-590+300	-590+300
Sand Amount, gms	60	60	60	60	60	60	60	60
Duration of Run, min.	30	25	21	30	30	30	22	12.77
Wt. of Coal Fed, gms	66.27	55.09	109.53	65.68	66.06	85.43	59.83	61.83
Vapour Residence Time, secs.	0.55	0.55	0.55	0.55	0.55	0.55	0.55	0.55
Moisture in Feed, wt.%	6.68	12.64	12.64	10.41	0	1.34	0.17	0.17
Ash in Feed, dry wt.%	6.70	6.01	6.01	5.12	2.63	2.78	2.58	2.58
Yields, wt.% maf								
Gas	22.53	22.70	13.04	20.29	21.32	20.64	19.52	10.64
Tar	8.71	11.45	11.31	12.92	12.07	13.23	14.39	13.55
Char	53.93	52.38	70.51	50.54	51.96	50.62	52.50	53.17
Water	14.65	12.01	2.22	13.56	13.53	14.46	11.10	9.28
Total Recovery	99.82	98.54	97.08	97.31	98.88	98.95	97.51	86.64
Yields of Gases, wt.% maf								
H_2	0.47	0.35	0.17	0.35	0.34	0.19	0.24	0.15
CO	6.49	6.32	2.56	6.21	6.76	7.33	6.79	6.63
CO_2	10.46	10.50	7.64	9.60	9.39	8.56	8.47	N.D.
CH_4	2.06	2.14	1.10	1.99	1.96	1.79	1.74	1.54
C_2H_4	0.64	0.55	0.15	0.54	0.63	0.52	0.49	0.46
C_2H_6	0.25	0.27	0.17	0.21	0.25	0.23	0.23	0.25
C_3	0.56	0.51	0.18	0.48	0.52	0.43	0.43	0.45
C_4+	1.61	2.06	1.08	0.89	1.48	1.58	1.13	1.15
Acid Used/wt. of Fresh Coal gm.eq/kg dry coal	0.0	0.397	0.397	0.583	0.959	1.185	1.736	1.736

* Run in CO_2 Atmosphere

accounts for most of this drop in gas production. It is possible that inhibition of the water gas shift reaction could be responsible for the higher CO/CO_2 ratio and lower H_2 yield noted. The increase in tar yield occurs as the mineral matter is removed from the coal. The steepest increase occurs with the greatest removal of mineral matter corresponding to the three successive washings with pH decreasing from 2.5 to 0.8. Table 8 shows that for these three washes the only cation appreciably removed from the coal is calcium. It is concluded, therefore, that this increase in tar yield following the three successive washings is due primarily to the removal of additional calcium from the coal. The increase in tar yield after the single milder washings (pH = 4 to pH = 2.5) could be due to the removal of calcium, magnesium or sodium from the coal or possibly to any combination of the three.

However, closer examination of the data suggests that the early tar increase following the milder acid washings does not appear to be a function of the sodium content, but could be due to removal of either calcium or magnesium or both.

The coal acid washed to a pH of 4.0 was also pyrolyzed at 550°C in Run 167. The lower temperature resulted in lower gas and water yields and higher char yields. Tar yield remained constant. It is interesting to note the difference between the gas compositions of the two runs (Run 166 at 650° and Run 167 at 550°C). Run 167 produced a higher percentage of CO_2 (38.65 vol.% vs. 27.91 vol.%), a lower percentage of CO (20.55 vol.% vs. 26.74

vol.%) and a slightly lower percentage of H_2 (18.51 vol.% vs. 21.07 vol.%). In Run 167 an inadvertent change in the feeder operation resulted in a very high feed rate (313 g/hr). This high feed rate subsequently resulted in 40 percent of the char produced blowing into the condensers.

Figure 8 shows the variation of yields of several products from the pyrolysis of acid washed Saskatchewan lignite coals. Yields of CO_2, H_2 and CH_4, decrease with increasing strength of acid treatment (i.e. decreasing cation content). Correspondingly, a slight increase in CO occurs while the water yield seems to fluctuate irregularly. Other workers have reported decreasing CO_2 with increasing CO and H_2O yields as cations are removed. Coupling this with a H_2 yield decrease suggests that cations catalyze the shift reaction.

Table 10 also shows that the increase in tar yield for acid extracted lignite is accompanied by both a lower gas yield and a lower char yield. Pyrolytic water yield is fairly constant except for the coal washed with the strongest acid. These runs (163, 164) show about a 30 percent reduction in water yield.

Run No. 164 used a CO_2 atmosphere in place of N_2 at 650°C. The results given in Table 10 do not show any significant changes due to the CO_2 if it is assumed that the CO_2 in the product gas would have the same yield as that produced in N_2 pyrolysis. This is in contrast to the high reactivity of Estevan lignite char in CO_2 at high temperatures (950°C) which was found in the thermo-gravimetric analysis.

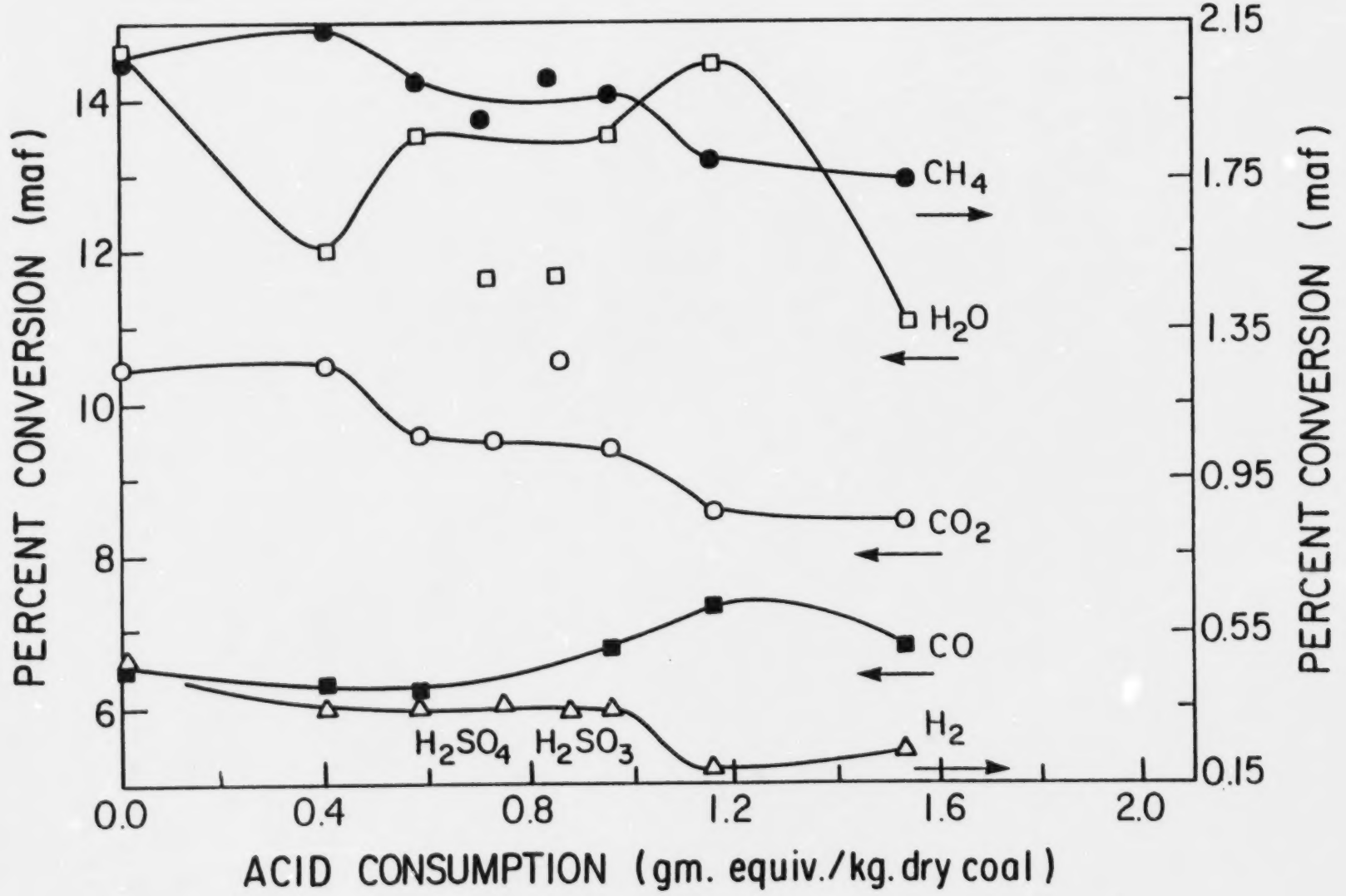

Figure 8 Gas Yields from Pyrolysis of Acid Washed Estevan Lignite #4, N_2, 650°C, 0.55 s.

It can be concluded from these pyrolysis results that even a mild acid wash with the minimum amount of acid will give close to the maximum benefit in increasing yields of pyrolysis liquids.

(d) Measurement of Carboxylate Groups in Lignite

The determination of carboxyl groups in the raw coal utilizes ion exchange (Morgan et al., 1981). The raw coal was first completely demineralized using the method of Bishop and Ward (1958) described previously. The H-form carboxyl groups resulting were then exchanged with barium acetate, releasing one mole of acetic acid for every carboxyl group exchanged. Barium hydroxide was then added to the solution until the pH was restored to the original value (8.25-8.30). The quantity of barium hydroxide utilized was used to calculate the number of carboxyl groups exchanged. To check this carboxyl group determination, the amount of barium exchanged onto the coal was determined by back exchanging with perchloric acid. The coal was first washed with sodium acetate to remove any residual barium acetate. The exchanged and washed coal was then boiled in perchloric acid and the solution was analyzed for barium by emission spectrometry. The carboxyl content was calculated by assuming two carboxyl groups to be exchanged with each barium ion. The carboxyl group content of demineralized Estevan lignite #4 was found to be 3.18 m equiv./g.maf by titration, which is the more reliable method, and 3.42 m equiv./g.maf by barium release.

By comparison, the total exchangeable cation content of the coal by ammonium acetate method was 1.38 m equiv./g.maf. This suggests that approximately 44 percent of the carboxyl groups were associated with cations. It has been reported by other workers that carbon dioxide yields from demineralized coal at high temperatures (~727°C) correspond almost exactly with carboxyl group content, that is one mole of carboxyl groups decompose to one mole of carbon dioxide. Upon cation addition to the de-mineralized coal, however, carbon dioxide yields exceeded this amount and some carbon dioxide must therefore originate from non-carboxyl oxygen. Carbon dioxide yields from pyrolysis of acid washed (pH = 0.8) Saskatchewan lignite coal at 650°C corresponded to only 60 percent of the measured carboxyl groups while carbon dioxide yield from the raw lignite accounted for about 72 percent. At higher temperatures carbon dioxide yields from acid washed coal would be expected to increase to an amount corresponding more closely with the carboxyl group content.

(e) Acid Washing of Lignite with H_2SO_4 and H_2SO_3

A raw Estevan lignite #4 sample was pyrolyzed (Run 171) under standard conditions (N_2, 650°C, 0.5 s residence time) to confirm the results of Run 160 reported in Table 10. Results from Run 171 are reported in Table 11. The results of Run 160 have been used as a basis from which to judge the effects of acid washing on the pyrolysis of Saskatchewan lignite coal. The tar yield of Run 171 (10.84%) is about 25 percent higher than that of Run 160. Therefore, the increased tar yield as a result of acid

Table 11

Pyrolysis of Acid Washed Estevan Lignite #4 with Different Acids

Run No.	171	175 Acid Washed H_2SO_3 pH = 3	176 Acid Washed H_2SO_4 pH = 3	165 Acid Washed HCl pH = 3.5
Temperature, °C	650	650	650	650
Coal Size, μm	-250+62	-250+62	-250+62	-250+62
Sand Size, μm	-590+300	-590+300	-590+300	-590+250
Sand Amount, gms	60	60	60	60
Duration of Run, min.	30	24.5	30	30
Wt of Coal Fed, gms	48.27	44.19	60.10	65.68
Vapour Residence Time, secs.	0.55	0.55	0.55	0.55
Moisture in Feed, wt. %	10.07	4.15	0.84	10.41
Ash in Feed, dry wt. %	7.64	5.52	5.28	5.12
Yields, wt. % maf				
Gas	23.12	22.54	19.73	20.29
Tar	10.31	12.63	12.25	12.92
Char	51.27	52.36	52.85	50.54
Water	10.38	11.64	11.51	13.56
Total Recovery	95.08	99.16	96.34	97.31
Yields of Gases, wt. % maf				
H_2	0.61	0.35	0.38	0.35
CO	5.87	7.14	5.99	6.21
CO_2	12.48	10.67	9.44	9.60
CH_4	2.08	1.97	1.82	1.99
C_2H_4	0.50	0.62	0.49	0.54
C_2H_6	0.28	0.24	0.22	0.21
C_3	0.45	0.52	0.42	0.48
C_4	0.85	0.86	0.87	0.89
BTX	not measured	0.17	0.11	not measured
H/C Ratio	0.78	0.77	0.74	0.81
Acid Consumed gm eq/kg dry coal	0	0.87	0.73	0.58

washing may not be as great as reported in previous tests. For example, whereas the tar yield for Run 165 is nearly 50 percent greater than that for Run 160, it is only 18 percent greater than that for Run 171. However, the conclusion that acid washing of lignite results in significantly increased yields of liquids is still true.

Also reported in Table 11 are results from the pyrolysis of Saskatchewan lignite samples washed with sulphuric and sulphurous acids. Results from the pyrolysis of a Saskatchewan lignite sample washed with a similar strength of hydrochloric acid (Run 165) are included for comparison. Sulphuric and sulphurous acids were selected to wash the lignite because they are less expensive than hydrochloric acid. If these cheaper acids result in similar increases in liquid yield then the economics of acid washing as a process alternative may become much more promising. The results in Table 11 show that the type of acid used to wash the coal had little effect on product yields. Tar yields varied from 12.25 percent for sulphuric acid washed lignite to 12.91 percent for hydrochloric acid treated lignite. Similarly, other product yields did not vary by more than would be expected due to experimental error. Sulphuric and sulphurous acid consumption (0.73 and 0.87 gm eq/kg dry coal) was similar to that of hydrochloric acid as was the reduction in ash content of the coal.

Figure 9 illustrates the dependence of tar yield on the degree of cation removal of the acid washed coals. The vertical axis is the fractional tar increase compared to the tar yield of

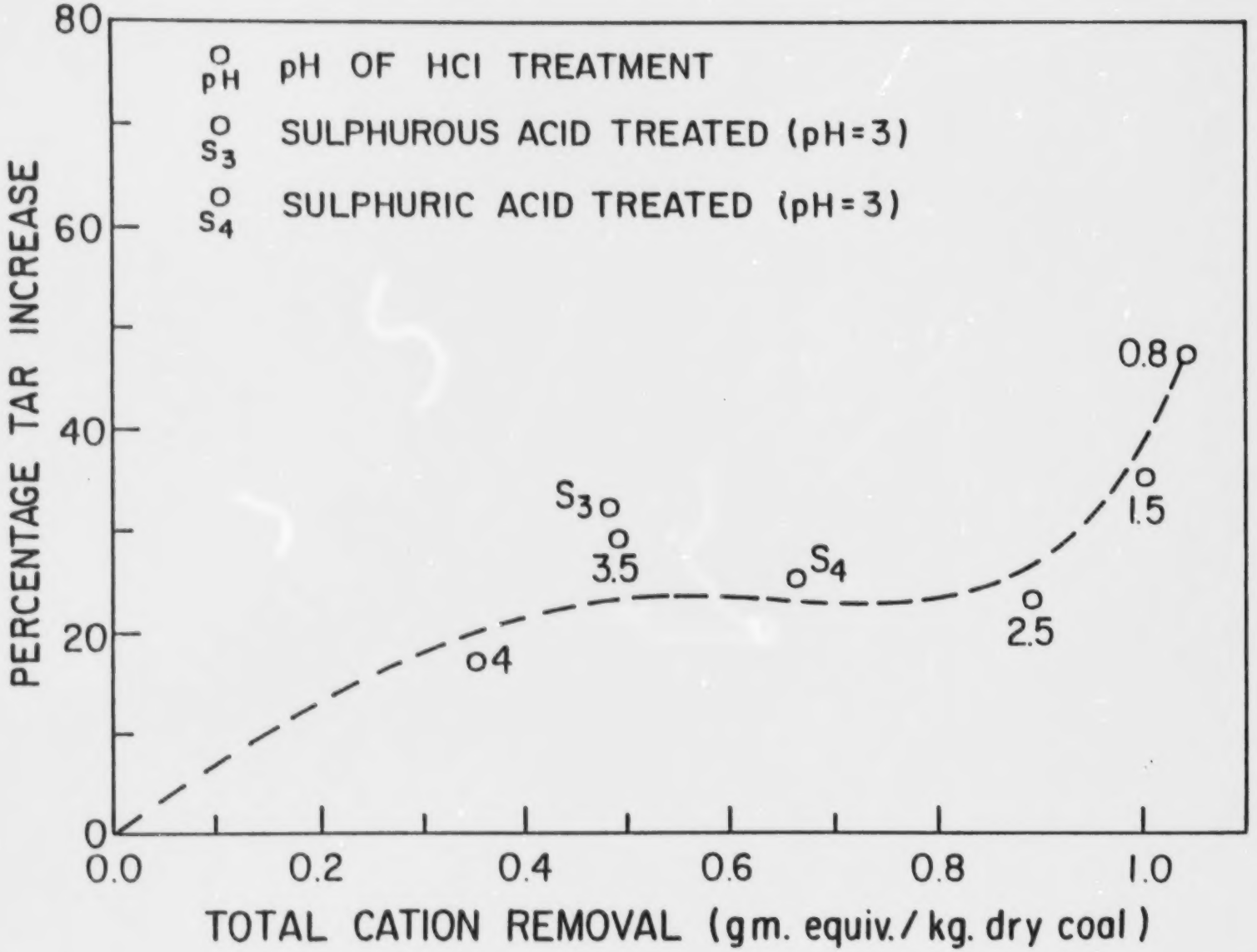

Figure 9 % Increase in Tar Yield vs. Amount of Cation Removal for Estevan Lignite #4, 650°C, N,, 0.55 s.

the raw coal. For acid washed Estevan lignites, the tar yields are compared to an averaged raw lignite tar yield of 9.78 percent (Runs 160 and 171). A direct relation appears to exist between acid consumption and increased tar yields regardless of acid type used for cation removal.

(f) **Analysis of Acid Washed Coals and the Pyrolysis Products**

The elemental analyses of raw coal used in Run 160 and the analyses for the acid washed feed coals for Runs 161-167 are presented in Table 12. A new analysis procedure prevented moisture loss from the sample during elemental analysis and resulted in improved hydrogen balances for Run 165 and Run 166. The hydrogen balances for Runs 163, 164 and 167 are somewhat low, however. A possible explanation for the low hydrogen balance of Run 163 is the relatively low water recovery. If a corrected water content was used to make up the total recovery to 100 percent, the hydrogen balance would become 99 percent. A similar argument would improve the hydrogen balance for Run 164, for which water yield was also relatively low (9.28%). Moisture in the gaseous product was not measured for Run 164 and it is expected that the addition of this water would improve both the overall and the hydrogen recoveries. The drop in the water yield for pyrolysis at 550°C (Run 167) compared to 650°C (Run 166) is roughly equal to the deviation in the hydrogen balance (23%) for Run 167. One would expect this difference to be made up by a higher char hydrogen content. The measured char hydrogen content for Run 167 is only slightly higher than would be expected for

Table 12

Acid Washed Estevan Lignite #4

Ultimate Analysis and Elemental Balance of Pyrolysis Products

-210 +62 μm, N_2 atmosphere, 0.55 s, 650°C

		Run 160	Run 165	Run 161	Run 162	Run 163	Run 164*	Run 166	Run 167**
Feed as is, or (maf)	C	59.86 (68.75)	58.84 (69.22)	63.36 (65.07)	61.90 (64.53)	66.34 (68.22)	66.34 (68.22)	58.29 (70.99)	58.29 (70.99)
	H	4.49 (4.36)	5.13 (4.67)	4.56 (4.68)	4.41 (4.44)	4.52 (4.63)	4.52 (4.63)	5.13 (4.54)	5.13 (4.54)
	N	1.57 (1.80)	1.34 (1.58)	1.61 (1.65)	0.91 (0.95)	1.40 (1.44)	1.40 (1.44)	1.51 (1.84)	1.51 (1.84)
	O	(25.1)	(24.53)	(28.6)	(30.1)	(25.7)	(25.7)	(22.63)	(22.63)
	Ash	6.25	4.59	2.63	2.74	2.58	2.58	5.25	5.25
	H/C	0.76	0.81	0.86	0.83	0.81	0.81	0.77	0.77
	H_2O	6.68	10.41	0.0	1.34	0.17	0.17	12.64	12.64
Tar	C	78.27	77.01	75.43	74.10	73.96	73.96	76.58	77.84
	H	7.47	7.37	7.46	7.36	7.62	7.87	6.94	8.47
	N	1.71	2.68	2.35	1.78	1.91	1.49	1.82	0.58
	O	12.5	12.9	14.8	16.8	16.5	16.7	14.66	13.11
	H/C	1.15	1.15	1.19	1.19	1.24	1.28	1.09	1.31
Char	C	81.29 (91.82)	84.20 (91.62)	83.94 (89.86)	88.05 (93.39)	87.92 (92.37)	88.58 (93.48)	81.26 (89.60)	80.22 (88.60)
	H	1.28 (1.45)	1.62 (1.76)	1.71 (1.83)	1.70 (1.80)	1.75 (1.84)	1.58 (1.67)	1.60 (1.76)	2.07 (2.29)
	N	1.31 (1.48)	1.04 (1.13)	1.24 (1.33)	1.29 (1.37)	1.10 (1.16)	1.19 (1.26)	1.46 (1.61)	0.80 (0.88)
	O	(5.25)	(5.49)	(6.98)	(3.44)	(4.63)	(3.59)	(7.03)	(8.23)
	Ash	11.47	8.10	6.59	5.72	4.82	5.24	9.31	9.46
	H/C	0.19	0.23	0.24	0.23	0.24	0.21	0.24	0.31
Gas	C	43.66	42.19	43.82	44.15	43.13		44.21	40.75
	H	6.58	5.91	6.09	5.29	5.37	8.59	6.33	5.44
	O	49.76	51.90	50.09	50.56	51.50		49.46	53.81
C Balance		98.15	94.77	98.83	102.26	99.02	N.D.	93.96	106.80
H Balance		106.59	97.70	99.17	103.30	94.05	84.17	99.32	77.16
Ash Balance		97.69	84.04	133.39	107.12	100.44	109.94	85.81	113.80
O Balance		112.26	110.20	98.31	90.44	90.49		125.17	80.85
Acid Consumed gm eq/kg		0	0.583	0.954	1.145	1.532	1.532	0.397	0.397

* Run in CO_2 Atmosphere

** Run at 550°C

pyrolysis at 650°C. Thus it is possible that the measured char hydrogen content for Run 167 is low resulting in a low hydrogen balance.

Table 13 presents the ultimate analysis of pyrolysis products and elemental balances of pyrolysis runs using raw lignite and sulphuric and sulphurous acids washed lignite. The carbon, hydrogen and oxygen balances are all very good (93% to 106%). The ash balances vary from 68 percent to 200 percent. These values are probably a result of the use of the somewhat inaccurate ash values measured for char by the elemental analyzer, which varied from 6.89 percent to 19.11 percent for the two acid washed coals. Ash measurements appear only to be reliable when using the standard method for ash determination, rather than the values obtained when using the very small samples required by elemental analysis. The H/C ratios of the acid washed coals were not much different than those of the raw coal. The H/C ratio varied from 0.78 for the raw lignite to 0.74 for the sulphuric acid washed lignite. For hydrochloric acid washed lignite the H/C ratio varied from 0.77 (pH=4) to 0.86 (pH=2.5). The H/C ratio of the tar was lower for the sulphuric and sulphurous acids washed samples (1.05 and 1.08) than for the raw lignite (1.15). Tars from hydrochloric acid washed lignite had H/C ratios which ranged from 1.09 (pH=4) to 1.24 (pH=0.8). Possibly a small decrease in the tar H/C ratio occurred with washing at low acidities while small increases occurred at the higher acidities. The composition of the char did not appear to be affected by acid washing, regardless of the type of acid used.

Table 13

Acid Washed Estevan Lignite #4

Ultimate Analysis and Elemental Balance of Pyrolysis Products

		N_2 atm, 0.55 s, 650°C		
		Run 171	Run 175 Washed H_2SO_3 pH = 3	Run 176 Washed H_2SO_4 pH = 3
Feed as is, or (maf)	C	63.65 (70.12)	62.62 (69.32)	63.51 (70.96)
	H	4.33 (4.55)	4.46 (4.43)	4.40 (4.38)
	N	1.13 (1.24)	0.75 (0.83)	1.26 (1.41)
	O	(24.09)	(25.42)	(23.25)
	Ash	7.45	5.29	5.24
	H_2O	1.78	4.15	0.84
	H/C	0.78	0.77	0.74
Tar	C	79.08	76.68	77.20
	H	7.59	6.72	6.97
	N	1.44	1.47	1.69
	O	11.89	15.13	14.14
	H/C	1.15	1.05	1.08
Char as is, or (maf)	C	82.11 (91.49)	85.52 (91.85)	75.45 (93.27)
	H	1.66 (1.85)	1.78 (1.91)	1.72 (2.13)
	N	1.14 (1.27)	1.61 (1.73)	1.39 (1.72)
	O	(5.39)	(4.51)	(2.88)
	Ash	10.25	6.89	19.11 [9.55] adjusted for 100% balance
	H/C	0.24	0.25	0.27
Gas	C	39.82	41.99	42.87
	H	6.40	5.50	5.68
	O	53.80	52.54	48.87
C Balance		93.02	96.99	96.63
H Balance		96.74	99.03	95.91
O Balance		106.21	104.07	95.82
Ash Balance		68.81	68.65	200.13 [100]
Acid Consumption gm eq/kg dry coal		0	0.87	0.73

Table 14 gives the proximate analysis (by TGA) of all the raw coals used in the acid extraction experiments, as well as the proximate analysis for an acid-washed (pH = 0.8) and a demineralized lignite. Apparently, acid washing of the lignite, or complete removal of the mineral matter, does not alter the volatile matter or fixed carbon content of the coal. It is also of interest to note that the fixed carbon content as determined by the TGA procedure with an N atmosphere is always about 2% to 4% less than the char yield obtained during pyrolysis at optimal conditions. Since any increase in tar yield as a result of acid washing is almost entirely at the expense of gas production, this conclusion holds for both raw and acid washed coals.

Table 14

TGA Proximate Analyses

	Moisture	Volatiles	Fixed Carbon	Ash
Raw Saskatchewan Lignite #4	6.66 0	41.66 47.83	45.42 52.15	6.24 0
Acid Washed (pH=0.8) Sask. Lignite #4	3.93 0	46.11 49.30	47.29 50.56	2.54 0
Demineralized Sask. Lignite #4	2.15 0	47.41 48.45	50.44 51.55	0 0
Raw Forestburg Sub-bituminous	11.36 0	38.33 46.05	44.73 53.74	5.41 0
Raw Hat Creek Sub-bituminous	7.67 0	28.46 56.43	21.82 43.27	41.90 0
Run 168 - Char from Pot	1.17 0	11.57 12.47	81.35 87.67	6.04 0
Run 168 - Char from Condensers	4.14 0	24.90 27.61	64.79 71.83	5.66 0

(ii) Acid Washing and Pyrolysis of Sub-Bituminous Coals

(a) Acid Extraction and Pyrolysis of Forestburg Sub-Bituminous Coal #2

The mineral matter contents of two acid washed Forestburg sub-bituminous coals are given in Table 15. The magnesium, sodium and potassium contents of the raw coal were obtained by exchange with ammonium acetate and are therefore considered to be present only as exchangeable cations associated with the organic matter in the coal. The calcium content of the raw coal was obtained by the analysis of the coal ash which gave a higher value than the exchangeable calcium determined by ammonium acetate exchange. Only 88 percent of the calcium determined by the ash analysis was exchangeable with ammonium acetate (see Table 15). The cation contents for the acid washed Forestburg samples were determined using the same method as for the Saskatchewan lignite samples. As expected the coal cation contents decreased with increasing severity of acid treatment. When washed at a pH of 1.5 calcium was completely removed from the coal and very little magnesium and potassium remained. Therefore, at this acidity, even the non-exchangeable form of calcium was removed from the coal. In contrast however, only 22 percent of the original sodium was removed with the same treatment. It can be concluded that the sodium present in both Forestburg sub-bituminous and Saskatchewan lignite coals is relatively difficult to remove by acid washing when compared to calcium, magnesium and potassium.

Table 15

Mineral Matter Content of Acid Washed Coal

Forestburg Subbituminous Coal -60 +230 mesh, 6.17% ash

(1) weight percent dry coal
(2) gr equiv/kg dry coal

	Raw by NH_4 Ac Ex.		pH = 3.5 HCl		pH = 1.5 HCl	
	(1)	(2)	(1)	(2)	(1)	(2)
Ca	0.75	0.37*	0.57	0.28	0.00	0.00
Mg	0.11	0.09	0.08	0.07	0.03	0.02
Na	0.53	0.23	0.41	0.18	0.42	0.18
K	0.03	0.008	0.02	0.005	0.01	0.003
Total	1.42	0.70	1.08	0.53	0.46	0.20

* From analysis of coal ash

Figure 10 shows a comparison of the degree of cation removal from the two coals as a result of acid washing. The similarity in behaviour suggests that lignites and sub-bituminous coals could be represented on such a plot by a family of curves, and that some more generalized representation may be possible when more data are available. In this event, predictions of the effectiveness of acid washing for cation removal might be possible.

Several pyrolysis runs using Forestburg sub-bituminous coal were made because of the unusually high tar yield obtained with the first test of the new #2 sample, as shown in the results of Run 158. The results of these tests are shown in Tables 16A and 16B along with the results of Run 168 showing the pyrolysis yields of acid washed Forestburg coal. The same pyrolysis conditions were used for Runs 158, 172, 177, 179 and 180. The total recovery of each run was very good (~100%) however the yields of individual products varied by as much as 5.5 percent. The tar yields of Runs 172, 177 and 180 agree very well (11.52%, 11.65% and 11.59%). The char and gas yields however vary by about five percent. These differences could be a result of differences in the extent of devolatilization of the chars. Char which has blown past the char pot and into the condensers has a higher volatile content than char which remains in the hot char pot. More char remained in the hot char pot during Run 177 than Run 172 and this could account for the larger gas yield and lower char yield of Run 177. However, it appears that acid washing Forestburg coal may result in significant increases in the yield of tar.

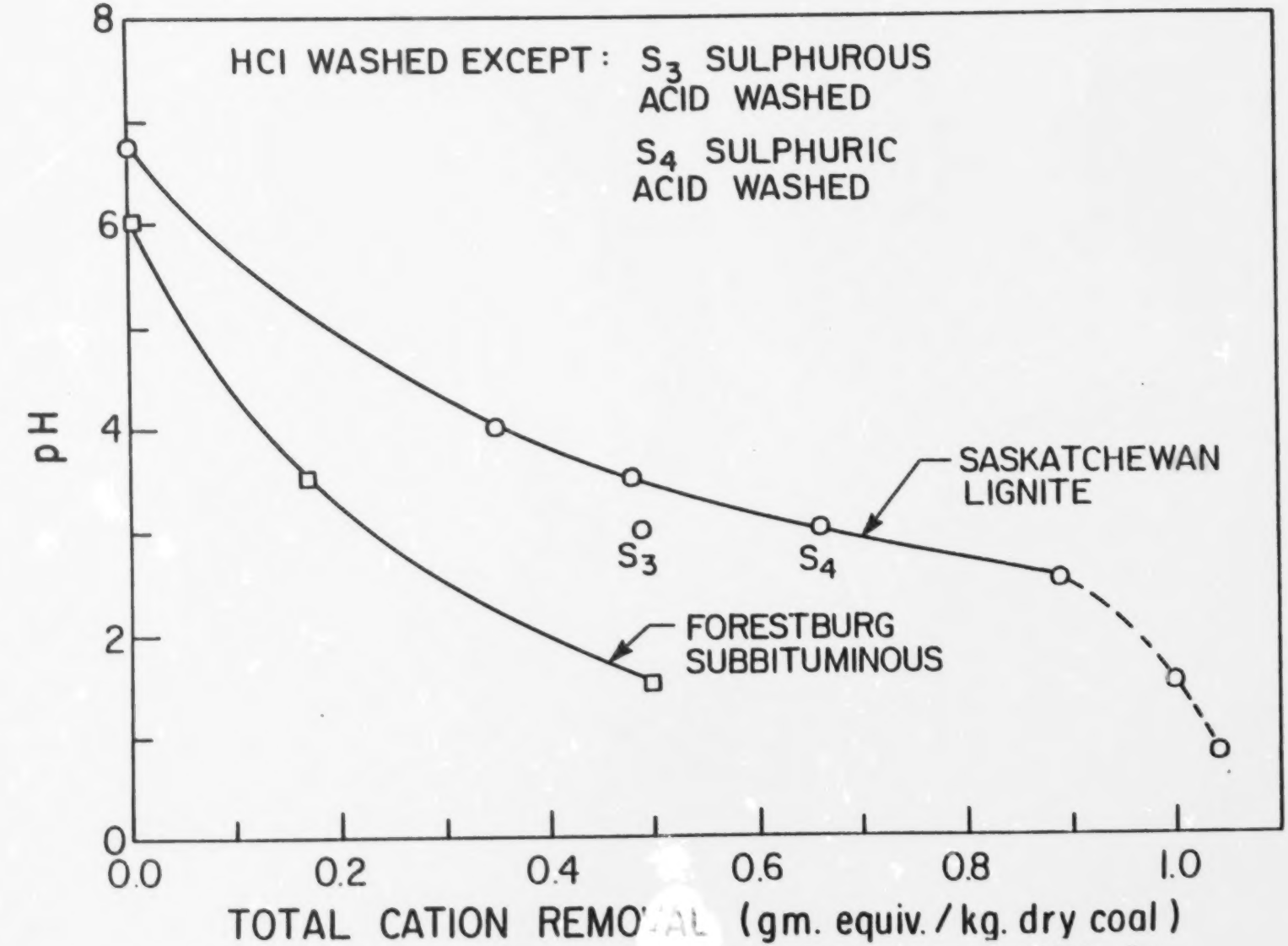

Figure 10 Dependence of Exchange Capacity on Wash Acidity for Two Coals - Estevan Lignite #4 and Forestburg Sub-Bituminous #2

Table 16A

Pyrolysis of Forestburg Sub-bituminous Coal #2

Run No.	158	172	177	168
Feed	Forestburg #2	Forestburg #2	Forestburg #2	Forestburg #2 Acid Washed HCl pH = 1.5
Temperature, °C	650	650	650	650
Coal Size, μm	-250	-250	-250	-250
Sand Size, μm	-590+300	-590+250	-590+250	-590+300
Sand Amount, gms	60	60	60	60
Duration of Run, min.	23	25.5	24	21.5
Wt. of Coal Fed, gms	27.53	77.78	59.47	71.52
Vapour Residence Time, secs.	0.55	0.55	0.55	0.55
Moisture in Feed, wt. %	11.06	4.33	4.33	2.25
Ash in Feed, dry wt. %	6.32	6.45	6.45	4.20
Yields, wt. % maf				
Gas	17.17	17.33	22.84	15.42
Tar	15.95	11.52	11.65	15.15
Char	57.34	61.02	57.94	60.22
Water	11.35	9.81	7.88	10.81
Total Recovery	101.81	99.69	100.31	101.60
Yields of Gases, wt. % maf				
H_2	0.35	0.23	0.99	0.21
CO	5.61	5.43	7.12	5.77
CO_2	6.74	7.82	9.39	5.30
CH_4	2.13	1.88	3.16	1.66
C_2H_4	0.65	0.47	0.47	0.49
C_2H_6	0.26	0.27	0.28	0.27
C_3	0.53	0.44	0.43	1.06
C_4	0.91	0.80	0.91	0.67
BTX	not measured	0.007	0.10	0.07
H/C Ratio	0.79	0.74	0.74	0.76
Acid Consumed gm eq/kg dry coal	0	0	0	0.78

Table 16B

Pyrolysis of Forestburg Sub-bituminous Coals
Use of Bench Scale Electrostatic Precipitator

N_2 atm, 0.55 s, 650° C

Run No.	179 Ice-Water Condensers	180 Electrostatic Precipitator
Temperature, °C	660	650
Coal Size, µm	-250 +62	-250 +62
Sand Size, µm	-590+300	-590+300
Sand Amount, gms	60	60
Duration of Run, min.	25	22.18
Wt. of Coal Fed, gms	63.25	56.53
Vapour Residence Time, secs.	0.55	0.55
Moisture in Feed, wt. %	4.33	4.33
Ash in Feed, dry wt. %	6.45	6.45
Yields, wt. % maf		
Gas	21.73	20.61
Tar	10.69	11.59
Char	54.61	55.92
Water	12.46	7.96
Total Recovery	99.49	96.08
Yields of Gases, wt. % maf		
H_2	0.90	1.34
CO	7.45	5.94
CO_2	8.04	7.77
CH_4	2.38	3.24
C_2H_4	0.90	0.59
C_2H_6	0.28	0.23
C_3	0.69	0.54
C_4	0.94	0.83
BTX	0.15	0.12

A sample calculation for the acid consumption values given for Run 168 is included in the Appendix.

An initial evaluation of an electrostatic precipitator for the recovery of coal pyrolysis products was made on the bench scale unit. The electrostatic precipitator used was of the two-stage type. In the first stage, or ionizing stage, corona discharge took place between two electrodes having a nonuniform field. Here the potential difference must be above that required for corona discharge. The second stage involved a relatively uniform electrostatic field in which charged droplets were caused to migrate to a collecting surface. The only voltage requirement in this stage was that no sparking occur, though higher voltages result in increased collection efficiency. In the bench scale electrostatic precipitator, the ionization stage consisted of a 13 cm long by 2.5 cm diameter glass tube in which the product stream flowed by a fine-wire discharge electrode and a large-diameter receiving electrode, separated by about 2.5 cm. The voltage applied was about 13.5 kV. The second stage or collecting unit consisted of a 28 cm by 6 cm diameter glass tube with a wire mesh plate about 25 cm long by 5 cm wide suspended in the middle of the tube. Two similar curved plates were located near the outside of the tube on opposite sides of the middle plate and with the opposite charge of the middle plate. The maximum voltage applied was about 6 kV but could be decreased if sparking occurred.

A pyrolysis run (180) with Forestburg sub-bituminous coal was made in which an electrostatic precipitator was followed by an ice-water condenser and a cotton-wool filter. The electrostatic precipitator worked well, however, sparking in the collecting unit forced a decrease in voltage which subsequently decreased collection efficiency. Despite this problem most of the tar was collected in the precipitator leaving the condenser and cotton-wool filter fairly clean. Only 15 percent of the total tar collected was in the cotton-wool filter compared with about 54 percent for a run using condensers alone. Table 16B compares results from two similar pyrolysis runs, one using an electrostatic precipitator and one using only ice-water condensers. Product yields were fairly consistent with the exception of the pyrolytic water yield which was 56 percent greater (12.46% vs. 7.96%) for Run 179 with the condensers than that of Run 180 with the electrostatic precipitator. Total recovery for Run 180 was slightly low (96.08%) and this could be due to underestimating the water yield. The yields of individual gas components for the two runs were very similar. The only notable differences were a slightly lower CO yield for Run 180 than Run 179 (5.94% vs. 7.45%) and a slightly higher H_2 yield for Run 180 (1.34% vs. 0.90%). The electrostatic precipitator appeared to work very well and an improved design to allow collection at maximum efficiency without sparking has now been developed.

In summary, it appears that Run 158 gave an erroneous tar yield, high by about 4 percent. Comparison of Run 168 using acid washed coal, with Runs 172, 177, 179 and 180 shows clearly that the removal of the cations associated with the coal organic matter increased the tar yield, mainly at the expense of the gas yield. Hence, the behaviour of the Forestburg sub-bituminous coal was very similar to that of the Estevan lignite.

(b) **Acid Extraction and Pyrolysis of Hat Creek Coal**

A sample of the high ash content Hat Creek sub-bituminous coal was given the same strength of acid treatment as the Forestburg sample. The pH of a Hat Creek sample slurried in distilled water was 3.6 compared to pH values of 6.2 and 6.8 for similar slurries of Forestburg and Saskatchewan lignite. Whether this acidic nature of Hat Creek coal is due to its organic or inorganic portion, or both, has not been determined. Once the slurry pH had been lowered to 1.5 by hydrochloric acid addition only 0.36 gram equivalents of acid per kilogram of dry coal (not ash free) were required to maintain this pH for 20 minutes. This acid consumption was only 46 percent of that required by Forestburg and only 31 percent of that used by Saskatchewan lignite at the same pH. This may indicate that the ion exchange capacity of Hat Creek coal is less than those of the Forestburg and the lignite samples. This is supported by the fact that the reduction in ash content of Hat Creek coal by acid washing to a pH of 1.5 was only 2 percent compared to reductions of 33 percent and 58 percent for Forestburg and Saskatchewan lignite coals respectively (see Tables 16A and 14, respectively).

Table 17 gives the results of an analysis of the cations associated with the organic matter of the coal as determined by the ammonium acetate exchange method, compared to results from the Estevan lignite #4 and the Forestburg #2 coals. Although the Hat Creek coal shows amounts of potentially exchangeable cations as large as that of Forestburg coal, this represents a much smaller fraction of the inorganic content in the case of the Hat Creek coal. The low acid consumption, in spite of the very high ash content of Hat Creek coal, is not unexpected when it is realized that much of the ash in this coal is in the form of finely disseminated clays. The effect of the nature of these clays (which would also probably have a small cation exchange capacity) can be seen from a test in which a sample of Hat Creek sub-bituminous coal fines (-325 mesh) was washed at a pH of 1.5 resulting in an acid consumption of 1.6 gm eq./kg dry coal. The coarser sample (-60 +200 mesh) similarly treated consumed only 0.36 gm eq./kg dry coal.

Shown in Table 18 are the results of the pyrolysis of Hat Creek sub-bituminous coal (Run 169). This high ash (50.3%) sub-bituminous coal produced more gas and water and less tar and char than the lower ash (6.32%) Forestburg sub-bituminous coal. The higher gas yield was largely due to a 90 percent increase in CO_2 yield as compared to Forestburg coal. The water yield was 77 percent greater and the tar and char yields were 54 and 17 percent less respectively than those reported for pyrolysis of Forestburg coal. As discussed previously, acid washing of Hat

Table 17

Cations Associated With Organic Matter in Coal

(1) weight percent dry coal

(2) $\frac{\text{cations by } NH_4Ac \text{ Exchange}}{\text{cations in Ash}} \times 100$

	Saskatchewan Lignite #4		Forestburg Subbituminous		Oxidized* Forestburg		Hat Creek Subbituminous	
	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)
Ca	1.07	102	0.66	88	0.63	84	0.64	N.D.
Mg	0.25	109	0.11	100	0.11	100	0.25	N.D.
Na	1.21	186	0.53	241	0.49	223	0.46	N.D.
K	0.06	150	0.03	300	0.03	300	0.05	N.D.
Total	2.59		1.33		1.26		1.40	

* Pre-oxidized in Air for 2 hrs. at 110°C

N.D. Cation content of ash not determined

Table 18

Pyrolysis of Hat Creek Sub-Bituminous Coal

Run No.	169	170
Feed	Hat Creek Rec'd Aug/83 (Ash 50.3%)	Hat Creek Acid Washed (pH=1.5)
Temperature, °C	650	650
Coal Size, m	-250+74	-250+74
Sand Size, m	-590+250	-590+300
Sand Amount, gms	60	60
Duration of Run, min.	30	20
Wt. of Coal Fed, gms	65.27	45.16
Vapour Residence time, secs.	0.55	0.55
Moisture in feed, wt. %	10.17	7.14
Ash in feed, dry wt. %	50.31	49.36
Yields, wt. % maf		
Gas	23.14	25.57
Tar	7.35	8.75
Char	47.51	48.03
Water	20.09	24.45
Total Recovery	98.09	106.80
Yields of Gases, wt. % maf		
H_2	0.47	0.35
CO	6.77	8.37
CO_2	12.90	12.60
CH_4	1.50	1.50
C_2H_4	0.31	0.44
C_2H_6	0.13	0.14
C_3	0.38	1.32
C_4+	0.65	0.71
H/C Ratio	0.95	
Acid Consumed gm eq/kh dry coal	0.0	0.36

Creek coal in a slurry of pH 1.5 did not result in any significant reduction in ash content of the coal. The acid consumed was 0.36 gm equivalents per kg of dry coal which is only 46 percent of that used by the Forestburg sample at the same pH. Thus the mineral matter of the Hat Creek coal is probably not in an ion exchangeable form and did not readily react with HCl during the acid washing procedure that was used, which would be expected if the coal contains a high clay content. The very large amount of CO_2 generated on pyrolysis of this coal and the high ash content both suggest that some of the mineral matter may be associated with carboxylate groups in the organic coal matter. However, the low acid consumption and the small apparent reduction in ash content after acid washing suggest that not much mineral matter is in ion exchangeable form.

Pyrolysis results for Run 170, shown in Table 18, indicate increases in gas, tar and water yields resulting in a total recovery of 106.8 percent. Because of the high recovery it is difficult to draw conclusions from this run, although it is expected that an overestimation of the water yield is responsible for most of the deviation from 100 percent. Gas analysis results show that only a small decrease in CO_2 yield occurred (0.3%) after acid washing compared to the larger decreases found for Forestburg (1.45%) and Saskatchewan lignite (1.9%). An increase in CO yield (1.6%) and a decrease in H_2 yield (0.12%) were also observed, although these were minor effects.

In agreement with the small amount of removal of cations from this coal as a result of acid washing, little increase in tar yield would be expected from the acid washed coal. Only a minor increase in tar yield was observed, and the tar yield from Hat Creek coal remains disappointing, despite its apparent high volatiles content.

(c) Pyrolysis of Acid Washed Sub-Bituminous Coal in CO_2

Previously, the effect of a CO_2 atmosphere on the yields of pyrolysis products from acid washed Estevan lignite #4 was shown to be negligible. Pyrolysis in CO_2 of a Forestburg acid washed coal has also been studied. Table 19 shows data from a run with an acid washed Forestburg sub-bituminous sample pyrolyzed in CO_2. Data from other appropriate runs are also presented for comparison. Run 77 was done without a cyclone and char pot and it is therefore not surprising that the char yield is high and the gas yield is low compared to Run 179. The other three runs employed a cyclone and char pot in which the pyrolysis char was kept at reactor temperature for the duration of the run allowing further devolatilization to proceed. The tar yield for Run 77 however is only about 1 percent less than that for Run 179.

The gas yield and total recovery for Runs 77 and 197 do not include the amount of CO_2 produced upon pyrolysis. This amount, based on the results of Runs 179 and 168, may vary from about 5 to 8 percent maf. Pyrolysis of the acid washed sub-

Table 19

Pyrolysis of Acid Washed Forestburg Subbituminous Coal in CO_2

Run No.	179	168	197	77 (March 25/83)
Feed	Raw	Acid Washed	Acid Washed	Raw
Atm	N_2	N_2	CO_2	CO_2
Temperature, °C	650	650	650	650
Coal Size, µm	-250 +62	-250	-250 +62	-149 +74
Sand Size, µm	-590 +300	-590 +300	-590 +300	-250 +149
Sand Amount, gms	60	60	60	14.98
Duration of Run, min.	25	21.5	19.5	30
Wt. of Coal Fed, gms	63.25	71.52	48.87	19.49
Vapour Residence Time, secs.	0.62	0.62	0.62	0.45
Moisture in Feed, wt. %	4.33	2.25	2.25	9
Ash in Feed, dry wt. %	6.45	4.20	4.20	5.5
Yields, wt. % maf				
Gas	21.58	15.42	12.09*	9.3*
Tar	10.69	15.15	13.18	9.5
Char	54.61	60.22	53.28	71.5
Water	12.46	10.81	14.62	5.3
Total Recovery	99.34	101.60	93.17	95.6
Yields of Gases, wt. % maf				
H_2	0.90	0.21	0.29	0.20
CO	7.45	5.77	7.77	6.66
CO_2	8.04	5.30	N.D.	N.D.
CH_4	2.38	1.66	1.94	1.30
C_2H_4	0.90	0.49	0.54	0.26
C_2H_6	0.28	0.27	0.25	0.21
C_3	0.69	1.06	0.46	0.27
C_4	0.94	0.67	0.75	N.D.
BTX	N.D.	0.07	0.10	0.4

N.D. Not Determined
* CO_2 not included

bituminous coal in a CO_2 atmosphere (Run 197) resulted in more gas (including estimated CO_2) and H_2O and less tar and char than pyrolysis in N_2. The tar was 2 percent less in CO_2 than in nitrogen and the char was 7 percent less. The CO yield was 2 percent higher for pyrolysis in CO_2 as opposed to nitrogen. Possibly the excess CO_2 favoured the production of H_2O and CO by the water-gas shift reaction. It is also possible that the CO_2 reacted with the char to form CO by the Boudouard reaction. Some combination of these reactions is the probable mechanism.

Pyrolysis of raw or acid washed sub-bituminous coal in a CO_2 atmosphere does not provide any advantages over that in a nitrogen atmosphere under the conditions studied. It is likely that higher temperatures are required for the CO_2 to participate in any pyrolysis (or gasification) reaction which will significantly affect the yield of products.

It is probably a reasonable conclusion that the increase in tar yield due to the removal of inorganic cations by acid washing will occur to about the same degree, regardless of the reaction atmosphere, for both lignites and sub-bituminous coals.

(d) Ultimate Analysis of Pyrolysis Products for Sub-Bituminous Coals

The ultimate analyses and elemental balances of the pyrolysis products are presented in Table 20 for Runs 168, 179 and 197 for the Forestburg coal, and Runs 169 and 170 for the Hat Creek coal. The acid washed Forestburg coal had a slightly

Table 20

Pyrolysis of Acid Washed Forestburg and Hat Creed Sub-Bituminous Coals
Ultimate Analysis and Elemental Balance of Pyrolysis Products
0.55 s 650°C

Run No.		179	168	197	169	170
Feed		Forestburg #2 Raw	Forestburg #2 Acid Washed (pH=1.5)	Forestburg #2 Acid Washed (pH=1.5)	Hat Creek Rec'd Aug. '83	Hat Creek Acid Washed (pH = 1.5)
Atm		N_2	N_2	CO_2	N_2	N_2
Feed as is, (maf)	C	63.51 (70.96)	64.50 (68.88)	64.50 (68.88)	29.52 (66.14)	28.38 (60.35)
	H	4.40 (4.38)	4.36 (4.39)	4.36 (4.39)	2.00 (4.48)	2.39 (5.09)
	N	1.26 (1.41)	1.42 (1.52)	1.42 (1.52)	0.42 (0.93)	0.77 (1.63)
	O	(23.25)	(25.21)	(25.21)	(28.45)	(32.93)
	Ash	6.17	4.11	4.11	45.19	45.84
	H_2O	4.33	2.25	2.25	10.17	7.14
	H/C	0.74	0.76	0.76	0.81	1.01
Tar	C	75.92	75.14	73.52	75.62	74.31
	H	6.60	6.92	7.07	6.70	6.55
	N	1.48	1.97	2.01	2.05	1.66
	O	16.00	15.97	17.40	15.63	17.48
	H/C	1.04	1.11	1.15	1.06	1.06
Char as is, (maf)	C	81.80 (88.91)	84.74 (92.52)	83.47 (90.35)	29.87 (89.62)	29.75 (90.37)
	H	1.54 (1.67)	1.72 (1.88)	1.64 (1.78)	0.65 (1.95)	0.75 (2.28)
	N	1.86 (2.02)	1.10 (1.20)	1.90 (2.06)	0.00	0.64 (1.91)
	O	(7.40)	(4.40)	(5.81)	(8.43)	(5.41)
	Ash	8.0	8.41	7.62	66.67	67.08
	H/C	0.23	0.24	0.24	0.26	0.30
Gas	C	44.19	46.95	53.92	37.98	40.85
	H	9.00	6.68	9.11	4.75	4.44
	O	46.81	46.37	36.98	57.27	54.71
C Balance		95.89	108.14	93.47	86.11	99.97
H Balance		114.11	101.93	104.68	110.26	109.88
O Balance		116.46	86.57	90.55	132.36	120.87
Ash Balance		71.42	123.78	100	97.98	99.08
Mass Balance		99.34	101.60	93.17*		

* CO_2 not determined

higher H/C ratio (0.76) than the raw coal (0.74). The acid washed Forestburg coal also produced tars with higher H contents (7% vs. 6.6%) and H/C ratios (1.13 vs. 1.04). Tar produced from Forestburg acid washed coal pyrolyzed in CO_2 had the highest H/C ratio (1.15) but also had a higher O content (17.4%). The H/C ratio of all three Forestburg chars was practically the same (0.23-0.24). Gas produced from raw Forestburg coal pyrolyzed in nitrogen had the highest H/C ratio (2.44). Elemental balances are quite good when compared with the mass balances.

The ultimate analyses of Hat Creek coal gave large variations in analyses. The high ash content of the coal (about 50%) and char (about 65%) makes the reproducing of results more difficult since relatively small variations in "as is" values become much larger when reported on a moisture and ash free basis. This problem is exacerbated by the small sample size required. These types of analytical problems may be responsible for the relatively poor elemental balances reported, although the values given are averages of three analyses. Also overestimated water yields may contribute to the high oxygen balances (~130%) and high hydrogen balances (~110%) reported. The high ash content of Hat Creek coal does however lead to good ash balances (~99%) which also indicates that char collection was fairly complete.

The H/C ratio of the Hat Creek acid washed coal appears to be much higher than that of the raw coal. However, in view of the small removal of cations by acid washing, this result is probably overstated. The tars from the raw and acid washed Hat

Creek coal showed virtually the same composition and H/C ratio, as would be expected from the pyrolysis results which showed only a small increase in tar yield as a result of acid washing. Similarly, char and gas elemental compositions showed little effect of the acid washing. As mentioned previously, the large amount of water of reaction obtained in pyrolysis (probably due to decomposition of the clay content), and the difficulty in accurately analyzing water yields probably account for much of the error in O and H balances.

(iii) Acid Washing and Pyrolysis of a Bituminous Coal

A 250 gram sample of Balmer low volatile bituminous coal was acid washed to a pH of 1.5 following the procedure described for the Estevan lignite. An analysis of the ash cation content, and of the exchangeable cations is given in Table 21, compared to two low rank coals. The low content of potentially exchangeable cations in the ash, and the small acid consumption during acid washing despite an ash content of 11.68% suggests that the ash is present largely as discrete mineral matter with possibly a high silica content.

Results from pyrolysis of the raw and acid washed samples are presented in Table 22. The agglomeration behaviour of the strongly caking Balmer coal did not seem to be altered by acid washing. Operating problems due to plugging of the cyclone and related tubing limited the coal which could be fed to 15-20 grams. Results show that the acid washed Balmer yielded nearly

Table 21

Coal Ash Cation Analysis

Element	Saskatchewan Lignite #4		Forestburg Sub-bituminous #2		Balmer Bituminous #2	
	wt.% of Ash	mm /g dry coal	wt.% of Ash	mm /g dry coal	wt.% of Ash	mm /g dry coal
Al	7.54	0.19	8.45	0.20	1.30	0.06
Fe	4.34	0.05	4.34	0.05	1.23	0.03
Ca	4.69	0.08	8.1	0.13	0.18	0.005
K	1.89	0.03	1.12	0.02	0.11	0.003
Na	6.51	0.19	0.21	0.01	0	0
Mg	2.89	0.08	1.32	0.03	0.23	0.01

Note: coal ashed at 950°C for approximately 2 hours in air.
Analysis was done using a direct coupled plasma emission spectrometer except calcium which was determined by atomic absorption.

Table 22

Pyrolysis of Acid Washed Balmer Bituminous Coal

Run No.	174	173
Feed	Balmer	Balmer Acid Washed HCl pH = 1.5
Temperature, °C	650	650
Coal Size, μm	-250 +62	-250 +62
Sand Size, μm	-590+300	-590+300
Sand Amount, gms	60	60
Duration of Run, min.	11.5	21
Wt. of Coal Fed, gms	21.22	15.51
Vapour Residence Time, secs.	0.55	0.55
Moisture in Feed, wt. %	1.61	0
Ash in Feed, dry wt. %	11.68	10.74
Yields, wt. % maf		
Gas	3.56	4.56
Tar	8.35	9.17
Char	84.28	75.44
Water	3.35	4.67
Total Recovery	99.54	93.84
Yields of Gases, wt. % maf		
H_2	0.15	0.27
CO	0.31	0.49
CO_2	0.44	0.47
CH_4	1.57	2.10
C_2H_4	0.13	0.18
C_2H_6	0.34	0.39
C_3	0.20	0.23
C_4	0.24	0.16
BTX	0.20	0.28
H/C Ratio	0.60	0.62
Acid Consumed gm eq/kg dry coal	0	0.17

30 percent more gas, 10 percent more tar and 10 percent less char than did the raw coal. The total recovery, however, was low at 93.84 percent and was most likely the result of low char recovery. The acid consumption of 0.17 gram equivalents per kilogram of dry coal was the lowest of any coal washed at any acid level during this investigation. The decrease in ash content to 10.74 percent from 11.68 percent was also low when compared to the ash reductions for Saskatchewan lignite and Forestburg sub-bituminous coals. Characteristics of Balmer bituminous coal suggest that acid washing should not affect its behaviour during pyrolysis. Most significantly, its low oxygen content (about 4%) would appear to preclude the presence of significant amounts of carboxyl groups, which are thought to be sites of ion exchange in low rank coals. Without these exchange sites, the metal cations that are thought to act most effectively as gasification catalysts would not be present in the organic matrix. Therefore, acid washing probably only accomplished a small dissolution of the relatively inert discrete mineral phase in the coal. The small amount of acid consumed during the washing seems to confirm the low ion exchange capacity of Balmer coal.

Scott (1984) has reported that for Balmer coal a sharp increase in tar yield in the 600° to 650°C range was accompanied by a sharp decline in char yield. Gas yields increased slowly over the same range. Thus for this coal a relatively small deviation in temperature (less than 25°C) in the range 600°-650°C could have resulted in fairly significant differences in product yields, and minor temperature variations between Run 173 and Run

174 could also have increased the normal experimental errors. Another possibility for increased yields of volatiles due to acid washing may be due to surface area effects. It was reported by Linares-Solano et al. (1979) that acid washing of higher rank coals resulted in more reactive chars due to changes in surface area and porosity on demineralization. Possibly similar effects could influence the other pyrolysis products of high rank coals.

From Table 22, it is clear, however, that acid washing of a caking bituminous coal has little effect in improving liquid tar yields, and has no discernible effect on the caking properties in the fluidized bed.

Table 23 gives the ultimate analyses for the raw and acid washed coal, as well as the elemental analyses of the pyrolysis products.

Ash balances for Balmer Runs 173 and 174 reported in Table 22 (about 88%) are not quite as good as those for Hat Creek. However, considering the low ash content (11.5%) and amount fed (15-20 gms), this is a satisfactory balance. Carbon balances are also satisfactory when compared with the overall material balances. Oxygen and hydrogen balances, however, are significantly high and low respectively. For Run 174, 99 percent of the oxygen originally present in the coal was recovered in the char. This unreasonably high value must by caused by either an underestimated oxygen content in the feed or an overestimated oxygen content in the char or both. It might be possible that the char picked up some oxygen prior to analysis and resulted in

Table 23

Ultimate Analysis and Elemental Balance of Feed and Pyrolysis Products for Balmer Coal #2

N_2 atm, 0.55 s, 650°C

		Run 174 Balmer	Run 173 Balmer Acid Washed (pH = 1.5)
Feed as is, (maf)	C	78.77 (90.64)	79.17 (88.70)
	H	4.11 (4.52)	4.10 (4.59)
	N	1.15 (1.32)	1.22 (1.37)
	O	(3.52)	(5.34)
	Ash	11.49	10.74
	H_2O	1.61	0
	H/C	0.60	0.62
Tar	C	80.94	82.77
	H	6.57	6.25
	N	2.08	2.10
	O	10.41	8.88
	H/C	0.97	0.91
Char as is, (maf)	C	80.53 (91.58)	81.61 (92.58)
	H	2.23 (2.54)	1.86 (2.11)
	N	1.53 (1.74)	1.62 (1.84)
	O	(4.14)	(3.47)
	Ash	12.07	11.85
	H/C	0.33	0.27
Gas	C	66.16	64.91
	H	20.06	21.46
	O	13.78	13.65
C Balance		95.20	90.63
H Balance		83.79	80.15
O Balance		223.39	153.54
Ash Balance		89.01	86.15
Acid Consumption gm eq/kg dry coal		0	0.17

an excess oxygen recovery. The oxygen recovered from pyrolytic water of Run 174 was also high (85% of the oxygen fed), which could be due to a slightly overestimated water content in the washings. The low oxygen content of Balmer coal means that small errors in analysis or recovery can lead to large deviations from 100 percent balance, particularly for analyses of the feed, tar and char in which oxygen content is determined by difference using the carbon, hydrogen and nitrogen contents. Hydrogen balances for the Balmer runs reported are slightly low (80-83%). As with oxygen determinations, the feed, tar and char analyses are the most likely source of error in hydrogen determinations.

(iv) Summary of Acid Washing Tests

Figure 11 shows how acid consumption varied with the pH of the acidic slurry, the type of coal, and the type of acid used. From results for Saskatchewan lignite it is apparent that acid consumption increased with increasing acidity of the wash solution. Acid consumption was to a major degree a measure of the extent of ion exchange which occurred, and therefore at higher acidities a greater degree of exchange occurred. Figure 11 also shows that the same degree of exchange occurred with sulphuric and sulphurous acids as with hydrochloric acid. At the same pH (pH=1.5), the acid consumption and thus the extent of ion exchange varied with the type of coal, and Figure 11 indicates the relative ion exchange capacities of the four coals. Estevan lignite had the highest exchange capacity and Balmer low volatile bituminous

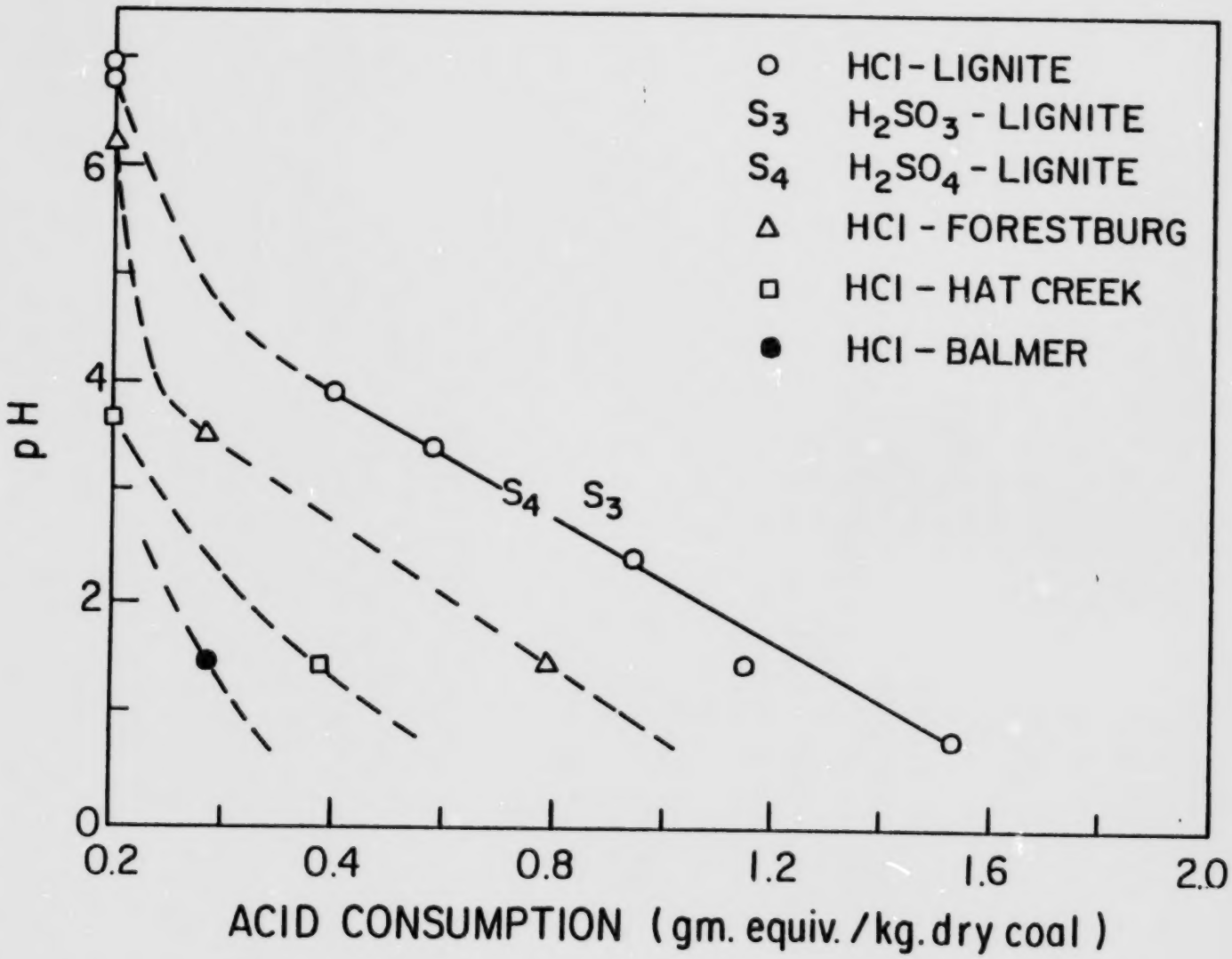

Figure 11 Dependence of Acid Consumption on Slurry Acidity for Different Coals and Acids

coal the lowest. If the Forestburg, Hat Creek and Balmer coals were washed to different slurry acidities a family of lines might result with each roughly parallel to that of Estevan lignite, as illustrated in Figure 11.

Although all the coals contain significant amounts of iron and aluminum, acid washing removed negligible amounts of these cations in each case. Ammonium acetate exchange also indicated that none of the coals contained any significant amount of ion exchangeable aluminum or iron. In the lignite, magnesium and calcium were totally exchangeable while sodium and potassium were only partially so. The exchangeable cation content of the sub-bituminous coals was less than that of the lignite in both cases despite the high ash content of the Hat Creek coal. Analytical problems were encountered in determining the exchangeable calcium in the acid washed lignites as well as the two raw sub-bituminous coals. The data for sodium and potassium contents indicate that acid washing removed exchangeable cations more readily than discrete minerals. This conclusion was also supported by the observations that magnesium and calcium were the most easily removed elements and were both totally exchangeable while aluminum and iron were the least easily removed and were not exchangeable at all.

Figure12 shows the fractional increase in tar yield for all the coals tested as a function of the acid consumption. An approximate correlation exists which shows that higher acid consumption results in larger fractional increases in tar yield

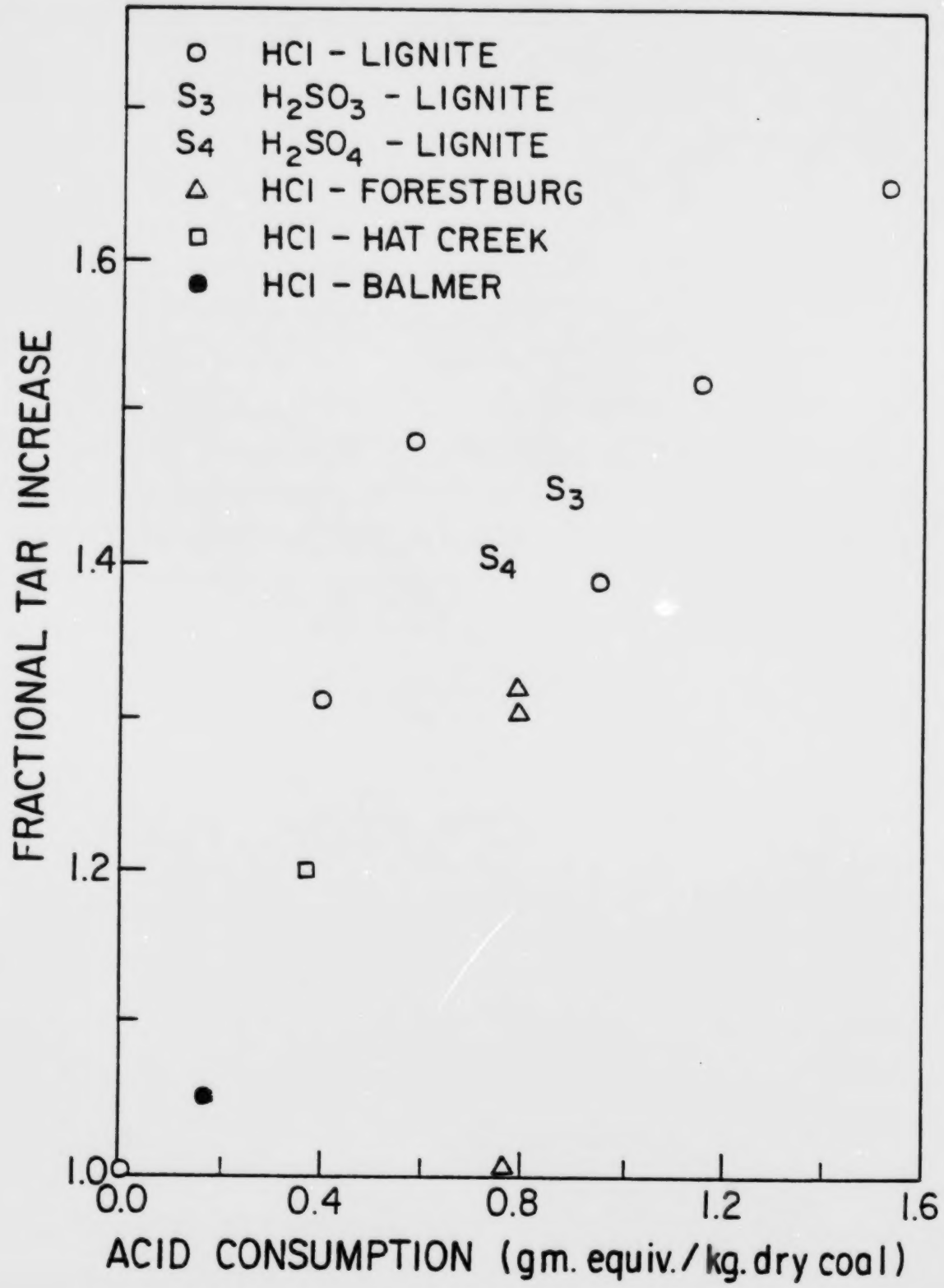

Figure 12 Dependence of Increase in Tar Yield on Acid Consumption for Different Coals

for the four coals tested. This trend appears to hold for all ranks of coal and any appropriate acid. Since acid consumption is a function of the fraction of alkali or alkaline earth cations which are in ion exchangeable form, for a coal to benefit from acid washing, it is necessary that it has a relatively high ion exchange capacity. This is consistent with the theory that the removal of exchangeable cations from the coal by acid washing results in the increased tar yields reported.

Further tests of low rank coals, especially lignites, are probably justified in order to verify the trend shown in Figure 12.

Acid washing of lignites, and to a lesser degree of subbituminous coals, leads to significant reductions in ash content. The replacement of mineral cations by hydrogen during acid washing might be expected to change the H/C ratio of products of pyrolysis. However, the additional H appears as an increase in liquid yield, which does also show a minor improvement in H/C ratio.

The presence of alkaline earth cations associated with carboxylic acid groups in the coal appears to lead to a decomposition of these groups preferentially to yield CO_2. When these cations are replaced by H, less CO_2 is produced and more liquid. The effect on char yield of the removal of Ca or Mg ions from the coal is uncertain, but is not a major effect.

(v) **Pyrolysis in Steam**

Pyrolysis of Estevanan lignite, Forestburg sub-bituminous and Devco bituminous coals in a steam-nitrogen gas mixture has been investigated.

Pyrolysis of the strongly caking Devco coal in steam at 650°C was attempted unsuccessfully. The coal continually plugged the injection tube despite air cooling of the tube. About a gram of coal reached the bed as evidenced by some agglomerated material discovered in the bed after the run. Although no products could be collected it can be concluded that steam probably does not prevent the agglomeration of the fluid bed when pyrolyzing caking coals.

Table 24 and Figure 13 present the data from the pyrolysis of Saskatchewan lignite in steam at three temperatures. Also shown are data from identical runs in nitrogen, so that a comparison between volatile product yields in steam and nitrogen can be made. The most significant effect of steam was the lower tar yield at each temperature. The tar yield in steam was fairly constant at around 7 percent compared to the tar yield in nitrogen which increased with temperature from 8.3 percent at 550°C to 10.3 percent at 650°C. Water yields also differed. However, due to the higher experimental error present for the product water determination in a steam run, these differences may be within the experimental error. Differences in the gas yield were not significant at 550°or 600°C, but at 650°C the gas yield in steam was 4 percent higher than in nitrogen. Figure 14

Table 24

Pyrolysis of Saskatchewan (Estevan) Lignite #4 in Steam

Run No.	190	171	189	194	188	193
Atm	Steam	N_2	Steam	N_2	Steam	N_2
Temperature, °C	650	650	600	600	550	550
Coal Size, μm	-250 +74	-250 +62	-250 +74	-250 +74	-250 +74	-250 +74
Sand Size, μm	-590 +300	-590 +300	-590 +300	-590 +300	-590 +300	-590 +300
Sand Amount, gms	60	60	60	60	60	60
Duration of Run, min.	30	30	30	30	31.5	30
Wt. of Coal Fed, gms	43.05	48.27	41.42	34.55	44.37	34.98
Vapour Residence Time, secs.	0.61	0.62	0.62	0.62	0.58	0.62
Moisture in Feed, wt. %	20.50	10.07	20.50	20.50	20.50	20.50
Ash in Feed, dry wt. %	7.01	7.58	7.01	7.01	7.01	7.01
Yields, wt. % maf						
Gas	27.34	23.12	20.82	21.31	(21.61)	(22.36)
Tar	(7.2)	10.31	7.07	8.77	7.26	8.32
Char	53.22	51.27	54.94	57.41	58.21	61.88
Water	(8.09)	10.38	11.46	11.23	12.32	9.51
Total Recovery	95.85	95.08	94.31	98.72	99.41	102.07
Yields of Gases, wt. % maf						
H_2	1.08*	0.61	0.37	0.35	(1.12)	(2.25)
CO	5.51	5.87	3.95	4.55	2.99	3.68
CO_2	16.53	12.48	13.07	13.31	11.04	11.67
CH_4	1.98	2.08	1.87	1.80	(5.45)	(3.75)
C_2H_4	0.53	0.50	0.32	0.27	0.19	0.23
C_2H_6	0.22	0.28	0.19	0.23	0.19	0.23
C_3	0.45	0.45	0.37	0.16	0.22	0.19
C_4	0.91	0.85	0.62	0.51	0.34	0.31
BTX	0.13	N.D.	0.08	0.12	0.09	0.05

N.D. Not Determined
* Estimate calculated from an assumed 8% v/v H_2 in Gas sample
Values in brackets are thought to be of low accuracy.

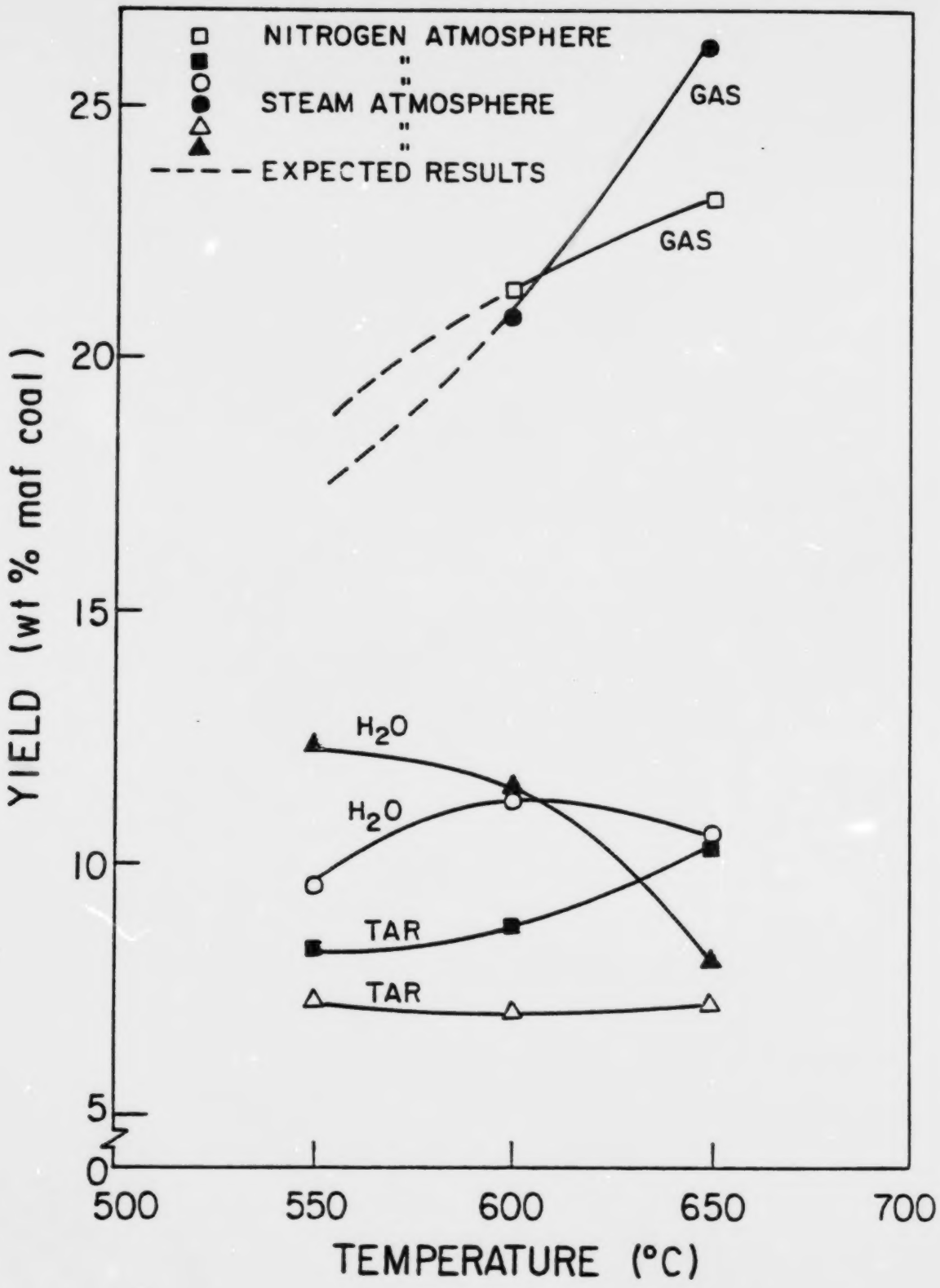

Figure 13 Product Yields From Steam Pyrolysis of Saskatchewan (Estevan) Lignite #4

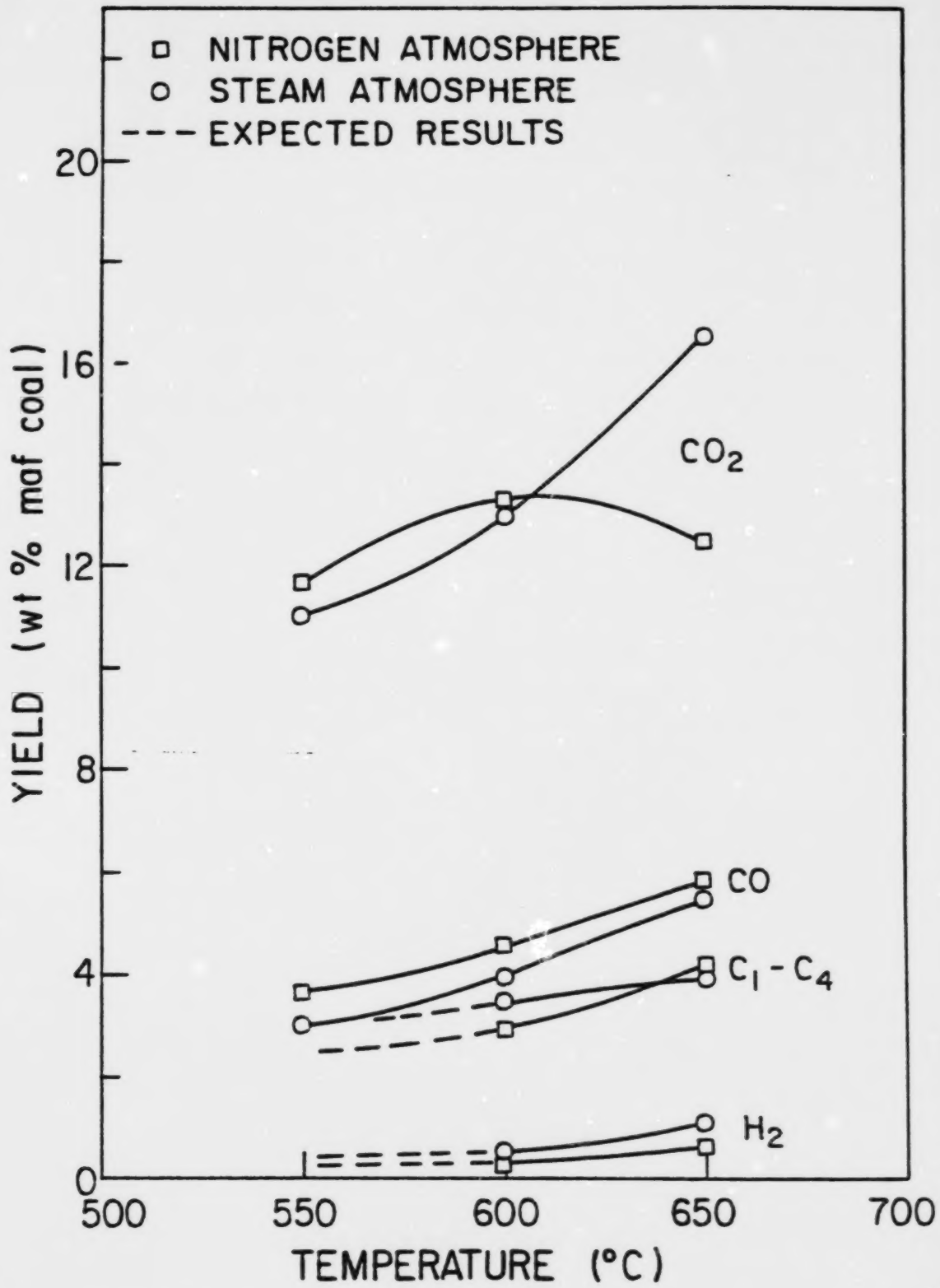

Figure 14 Gas Component Yields From Steam Pyrolysis of Saskatchewan Lignite #4

presents a comparison of the major gas component yields for pyrolysis in steam and nitrogen. The 4 percent increase in gas yield at 650°C for steam pyrolysis was due to an increase in CO_2 production. The other major gas components were practically identical to the yields in nitrogen. It is possible that the excess steam may have promoted the water-gas shift reaction, producing more CO_2 and H_2. The H_2 yield was slightly higher for Run 190 in steam compared to Run 171 in N_2. It is not likely at these low temperatures that the carbon-steam reaction producing CO and H_2 would be significant. Although for both runs at 550°C the data in Table 24 indicate relatively high H_2 and CH_4 yields compared to other runs, this is likely due to the contamination of the apparatus prior to the run. The expected values should be equal to or slightly less than those at 600°C. The dashed lines in Figures 13 and 14 represent these expected values. Yields of BTX were low and did not differ very much for steam or nitrogen. Char yields decreased with temperature but did not appear to be affected by a steam atmosphere as opposed to a nitrogen atmosphere. It is interesting that at 650°C the loss in tar yield in a steam atmosphere corresponded to the increase in gas yield (mainly H_2 and CO_2), suggesting some degree of steam reforming of the tar to yield H_2 and CO_2.

Table 25 gives the ultimate analyses and elemental balances of the pyrolysis products for the lignite runs in steam and nitrogen. The feed coal was the same for all runs except that for Run 171 the feed was dried to 10 percent moisture. For all other runs the moisture content was 20.5 percent. The ultimate

Table 25

Pyrolysis of Saskatchewan (Estevan) Lignite #4 in Steam

Ultimate Analysis and Elemental Balances of Pyrolysis Products

		Run 190 Steam	Run 171 N_2	Run 189 Steam	Run 194 N_2	Run 188 Steam	Run 193 N_2
Feed (maf)	C			70.12			
	H			4.55			
	N			1.24			
	O			24.09			
	Ash			7.45			
	H_2O	20.50	10.07	20.50	20.50	20.50	20.50
	H/C	0.78	0.78	0.78	0.78	0.78	0.78
Tar, maf	C	78.70	79.08	78.64	76.24	74.69	77.51
	H	7.40	7.59	7.61	7.88	7.65	7.89
	N	1.98	1.44	1.31	1.57	0.94	1.77
	O	11.92	11.89	12.44	14.31	16.72	12.83
	H/C	1.13	1.15	1.16	1.24	1.23	1.22
Char as is, (maf)	C	81.84 (91.54)	82.11 (91.49)	81.01 (90.20)	77.74 (86.38)	79.74 (88.64)	75.69 (83.71)
	H	1.58 (1.77)	1.66 (1.85)	1.91 (2.13)	1.85 (2.06)	2.37 (2.63)	2.27 (2.51)
	N	1.28 (1.43)	1.14 (1.27)	1.16 (1.29)	1.18 (1.31)	1.15 (1.28)	1.21 (1.34)
	O	(5.26)	(5.39)	(6.38)	(10.25)	(7.45)	(12.44)
	Ash	10.60	10.25	10.19	10.00	10.04	9.58
	H/C	0.23	0.24	0.28	0.29	0.36	0.36
Gas	C	37.23	39.82	38.27	37.52	42.49	37.61
	H	6.94	6.40	5.04	4.62	12.32	14.90
	O	55.84	53.80	56.69	57.85	45.18	47.49
C Balance		93.64	93.02	91.57	93.08	95.72	96.19
H Balance		94.48	96.74	89.93	91.55	135.10	145.17
O Balance		108.18	106.21	109.62	118.02	109.17	112.98
Ash Balance		85.42	68.81	84.39	85.96	87.50	88.19
Mass Balance		95.85	95.08	94.31	98.72	99.41	102.07

analyses of the tar products are fairly constant. The H content may be slightly lower for tar produced in steam as opposed to nitrogen, however, the difference is only about 0.2 percent. The tar oxygen content seemed to decrease with increasing temperature although definite trends are difficult to identify. The char H contents definitely decreased with increasing temperature as did the H/C ratios. Differences in the char H content and H/C ratio between steam and nitrogen runs were very small. Similarly, char oxygen contents decreased with increasing temperature and chars produced in steam had lower oxygen contents than chars produced in nitrogen. The only significant conclusion from the gas ultimate analysis is that the usually high H contents of Runs 188 and 193 (12.3% and 14.9%), which contributed to high overall H balances (135% and 145%), are probably due to contamination of the apparatus. All other elemental balances are very reasonable when compared to the mass balances. (The same pyrolysis apparatus was being used concurrently by another worker using pure hydrogen atmospheres.)

Forestburg sub-bituminous coal was also pyrolyzed in steam at three temperatures. Data from these runs as well as similar runs in nitrogen are presented in Table 26 and are shown in Figures 15 and 16. The char yields decreased by about 5 percent as the temperature increased from 550°to 650°C. However, there was little difference between char yields produced in steam and those produced in nitrogen. Figure 15 displays the other product yields as a function of temperature and pyrolysis atmosphere. Tar yields for both nitrogen and steam runs were very similar at

Table 26

Pyrolysis of Forestburg Subbituminous Coal in Steam

Run No.	191	179	185	196	186	195
Atm	Steam	N_2	Steam	N_2	Steam	N_2
Temperature, °C	650	650	600	600	550	550
Coal Size, μm	-250 +62	-250 +62	-250 +62	-250 +62	-250 +62	-250 +62
Sand Size, μm	-590 +300	-590 +300	-590 +300	-590 +300	-590 +300	-590 +300
Sand Amount, gms	60	60	60	60	60	60
Duration of Run, min.	26	25	28.5	21	29.5	19
Wt. of Coal Fed, gms	65.19	63.25	67.91	35.11	82.80	44.55
Vapour Residence Time, secs.	0.72	0.62	0.66	0.62	0.61	0.62
Moisture in Feed, wt. %	4.33	4.33	4.33	4.33	4.33	4.33
Ash in Feed, dry wt. %	6.45	6.45	6.45	6.45	6.45	6.45
Yields, wt. % maf						
Gas	18.01	21.73	15.98	14.78	14.96	(19.01)
Tar	8.49	10.69	9.30	9.71	8.31	8.65
Char	55.58	54.61	56.50	59.84	61.60	62.42
Water	11.51	12.46	14.15	15.31	15.23	14.22
Total Recovery	93.58	99.49	95.93	99.64	100.10	104.30
Yields of Gases, wt. % maf						
H_2	0.31	0.90	0.17	0.19	0.09	(0.88)
CO	5.32	7.45	4.35	3.79	3.52	4.01
CO_2	8.85	8.04	8.44	7.92	8.61	8.40
CH_4	1.77	2.38	1.66	1.59	1.52	(4.76)
C_2H_4	0.49	0.90	0.30	0.22	0.20	0.15
C_2H_6	0.22	0.28	0.21	0.19	0.27	0.22
C_3	0.42	0.69	0.30	0.29	0.26	0.22
C_4	0.64	0.94	0.53	0.51	0.44	0.34
BTX	N.D.	0.15	0.04	0.08	0.04	0.03

N.D. Not Determined
Bracketed values thought to be in error

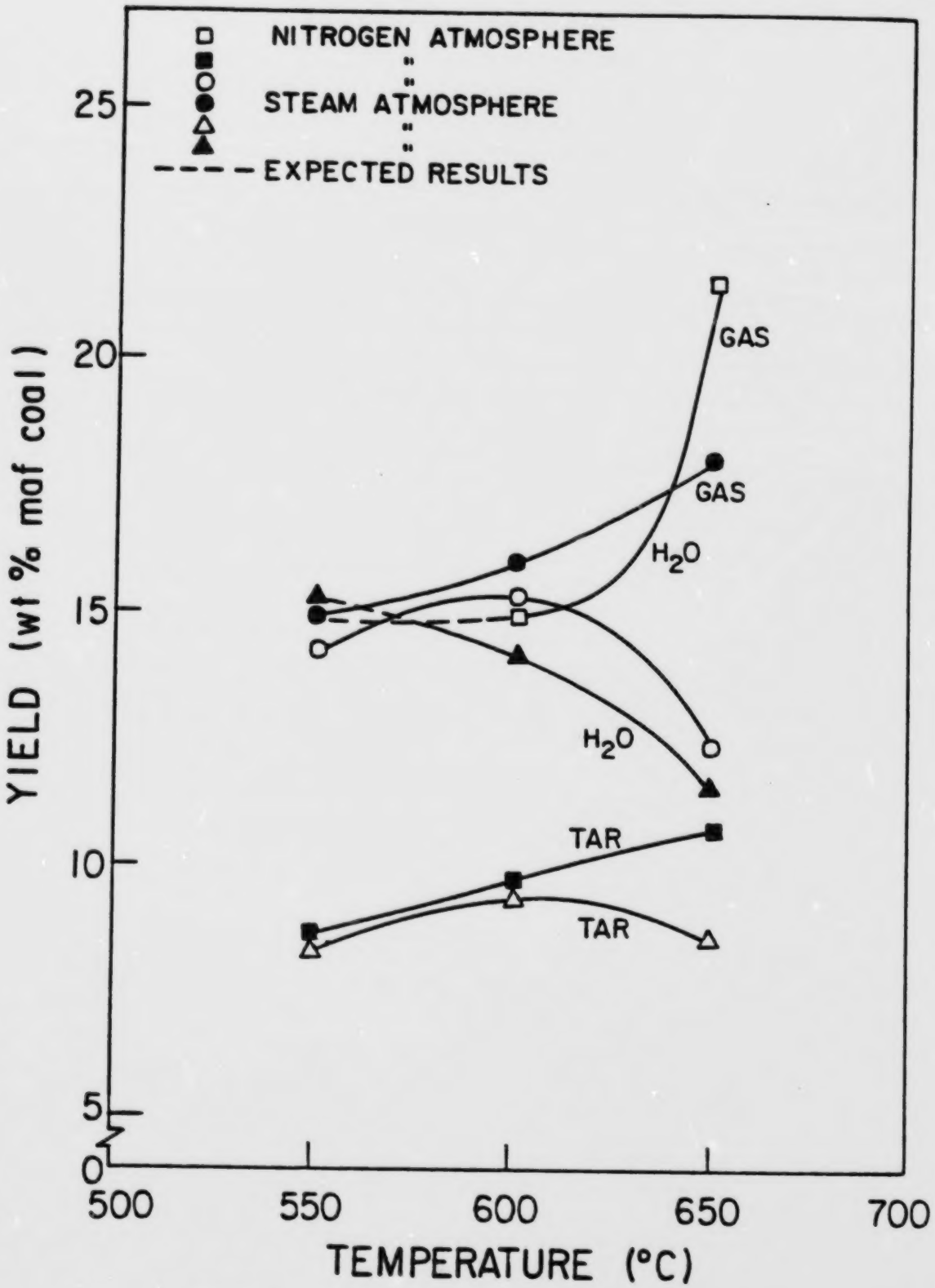

Figure 15 Product Yields From Steam Pyrolysis of Forestburg Sub-Bituminous Coal #2

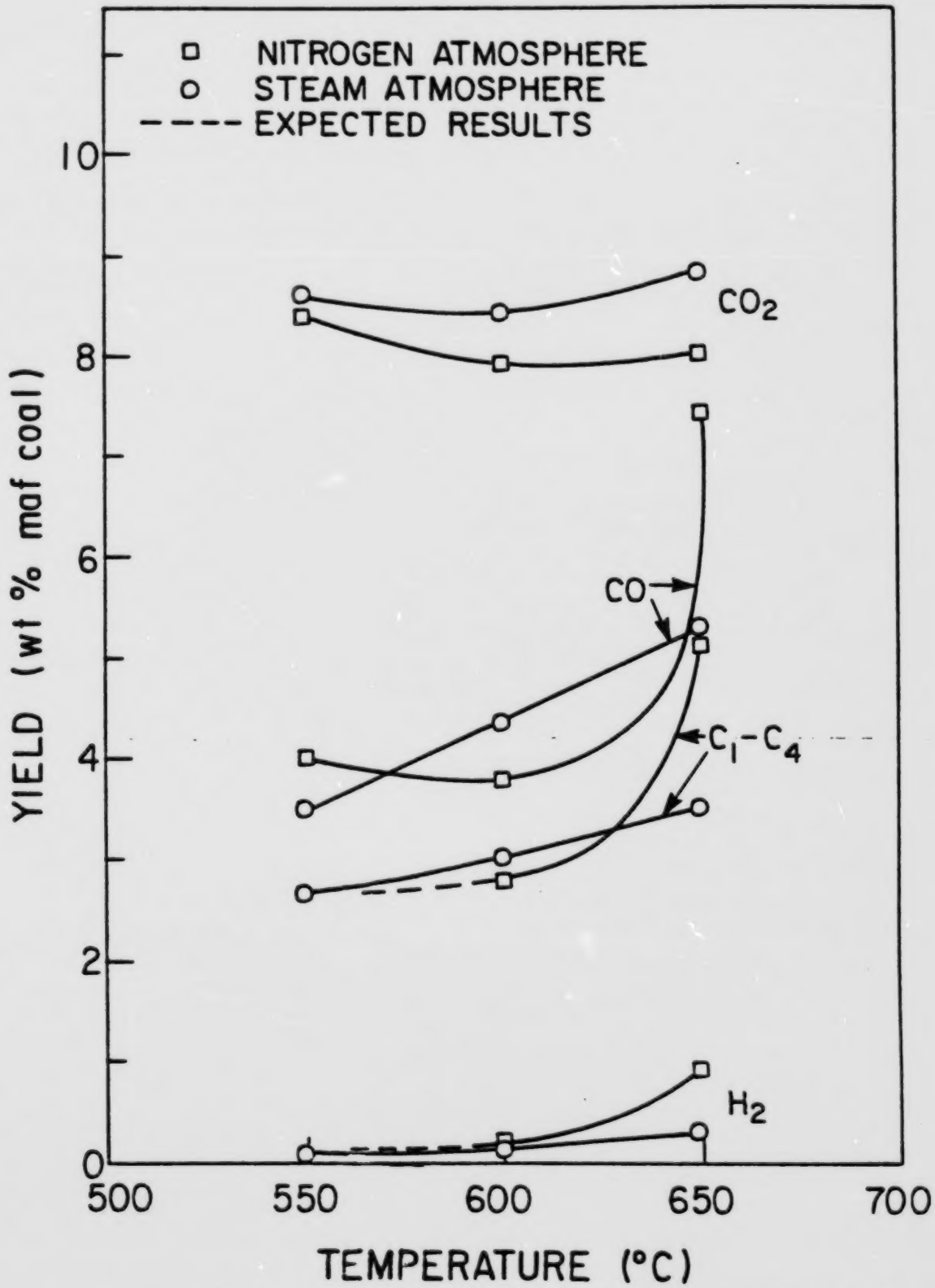

Figure 16 Gas Component Yields From Steam Pyrolysis of Forestburg Sub-Bituminous Coal

550° and 600°C but at 650°C the yield of tar produced in steam was 2 percent less than that for the tar produced in nitrogen. The poorer mass balances in the steam system makes these yield comparisons uncertain, however. Water yields for steam and nitrogen runs were within about 1 percent of each other. The data reported in Table 26 for Run 195 indicate relatively high CH_4 and H_2 yields compared to other runs. These values are thought to be due to contamination of the apparatus prior to the run. The expected values are thought to be similar to those of Runs 186 and 196. The dashed curve in Figure 16 represents these corrected values. At 650°C the gas yield in nitrogen was almost 4 percent higher than the gas yield in steam. The gas component yields from Forestburg coal pyrolyzed in steam and in nitrogen atmospheres are compared in Figure 16. Note that the correction in the CH_4 and H_2 yields at 550°C in a nitrogen atmosphere has caused the corresponding curves to approach those for steam at the low end of the temperature range. C_1 to C_4 hydrocarbons were about 3 percent higher in nitrogen at 650°C than they were in steam. The sample pyrolyzed in nitrogen at 650°C produced 0.6 percent more H_2 than the sample pyrolyzed in steam. The yield of CO at 650°C was about 2 percent higher for the nitrogen run compared to the steam run. CO_2 yields at 550°C were about the same for the two runs but at 650°C the CO_2 yield in steam was about 0.8 percent higher than that in nitrogen.

Table 27 gives the ultimate analyses and elemental balances of the pyrolysis products from Forestburg coal pyrolyzed in both steam and nitrogen. The feed analysis was the same for all the runs. The tar O content increased slightly with increasing temperature. The tar H content decreased with increasing temperature as did the H/C ratio. For the runs at 550° and 600° C the tar H/C ratio did not vary by more than 0.02 at each temperature with pyrolysis atmosphere. However for tar produced at 650 C the tar H/C ratio for the steam run is 0.09 higher than for the nitrogen run, due to the apparent low H content for the tar of Run 179 (N_2, 650° C), which may be in error. The char H content also decreased with increasing temperature as did the char H/C ratio. For all three temperatures the char H/C ratio did not vary by more than 0.02 with pyrolysis atmosphere at a given temperature. The high gas H content of Run 195 (11.6%) which results in a high H balance (139%) was due to contamination of the experimental apparatus with CH_4 and H_2 from an earlier test. The other gas H contents were consistently lower (5%) except for that of Run 179 (9%). The H balance for this run was slightly high (114%) but not unreasonable. The relatively high gas H content may balance the low tar H content for Run 179. The elemental balances were all reasonable when compared to the mass balances.

The major effect of steam on the pyrolysis of a lignite and a sub-bituminous coal at temperatures from 550° to 650° C appears to be a reduction in the tar yield particularly at 650° C, apparently due to gas formation due to a tar-steam reaction. For

Forestburg sub-butuminous coal the temperature at which the maximum tar yield occurs dropped from 650°C in nitrogen to 600°C in steam. For Saskatchewan lignite the tar yield in steam is constant from 550° to 650°C while in nitrogen it increases by 2 percent. The only other significant difference that is consistent for both coals is an increased CO_2 yield for steam pyrolysis compared to nitrogen. From these tests it is evident that steam provides no significant benefits in the pyrolysis of lignite or of sub-bituminous coals under the conditions studied.

Table 27

Pyrolysis of Forestburg Subbituminous Coal in Steam

Ultimate Analysis and Elemental Balances of Pyrolysis Products

		Run 191 Steam	Run 179 N_2	Run 185 Steam	Run 196 N_2	Run 186 Steam	Run 195 N_2
Feed (maf)	C			70.96			
	H			4.38			
	N			1.41			
	O			23.25			
	Ash			6.17			
	H_2O			4.33			
	H/C			0.74			
Tar	C	76.18	75.92	77.21	75.98	76.69	75.88
	H	7.19	6.60	7.67	7.66	8.26	8.01
	N	1.14	1.48	0.90	1.49	0.92	1.75
	O	15.49	16.00	14.22	14.87	14.13	14.36
	H/C	1.13	1.04	1.19	1.21	1.29	1.27
Char as is, (maf)	C	82.57 (91.16)	81.80 (88.91)	81.04 (90.80)	78.64 (86.98)	79.53 (87.64)	75.88 (83.17)
	H	1.73 (1.91)	1.54 (1.67)	1.89 (2.12)	1.98 (2.19)	2.44 (2.69)	2.35 (2.58)
	N	1.21 (1.34)	1.86 (2.02)	1.59 (1.78)	1.32 (1.46)	1.81 (1.99)	1.76 (1.93)
	O	(5.59)	(7.40)	(5.30)	(9.37)	(7.68)	(12.32)
	Ash	9.42	8.0	10.75	9.59	9.25	8.76
	H/C	0.25	0.23	0.28	0.30	0.37	0.37
Gas	C	41.67	44.19	40.76	40.91	40.00	44.12
	H	5.80	9.00	5.16	5.19	4.52	11.62
	O	52.52	46.81	54.08	53.90	55.48	44.25
C Balance		92.39	95.89	91.70	92.91	94.19	95.24
H Balance		91.80	114.11	98.68	92.60	108.09	139.49
O Balance		103.95	116.46	109.73	121.02	119.37	125.87
Ash Balance		85.41	71.42	98.85	92.67	91.88	88.05
Mass Balance		93.58	99.49	95.93	99.64	100.10	104.30

vi) Pilot Plant Pyrolysis Tests

The process flow sheet for the 2 kg/h pilot plant unit was shown in Figure 2, and a description of the unit, and the product collection system was given in a previous section. The lignite used was a sample from the Coronach (Saskatchewan) lignite strip mine, located in the southern border area with North Dakota. (The ultimate analysis of this coal is shown in Table 30.)

A comparison of results obtained from the pyrolysis of Saskatchewan (Coronach) lignite coal using both the bench scale unit and the pilot plant unit is shown in Table 28 for runs at different particle sizes. There are some significant differences. First note that the coal size range for the bench scale run was -250 +74 μm whereas the coal size for the pilot plant run included everything less than 3175 μm (1/8"). Table 29 gives a complete particle size distribution of the pilot plant feeds used. The total recovery of 108 percent for Pilot Plant Run P-55 cast some doubt on the values given in Table 28 for the individual product yields. Experience from additional pilot plant runs with coal showed that the conditions of Run P-55 would cause sand to be blown from the fluid bed into the char pot during a run, resulting in an overestimation of the char yield, and this was probably responsible for the high total recovery for Run P-55. Reducing the total recovery to 100 percent by reducing the reported char yield by 8 percent results in a char yield which is more consistent with results from similar runs. Comparing the corrected product yields of pilot plant Run P-55 to

Table 28

Pyrolysis of Saskatchewan (Coronach) Lignite Coal
Comparison of Bench Scale Unit and Pilot Plant Unit

Run No.	178	P-55	P-65
Feed	Bench Unit N_2 atm	Pilot Plant N_2+recirculated gas	Pilot Plant N_2+recirculated gas
Temperature, °C	590	585	647
Coal Size, μm	-250 +74	-3175	-1680
Sand Size, μm	-590 +300	-840 +590	-840 +590
Sand Amount, gms	60	2100	2100
Duration of Run, min.	35.0	187	133
Wt. of Coal Fed, gms	47.39	4505.5	3005.1
Vapour Residence Time, secs.	0.62	0.54	0.50
Moisture in Feed, wt. %	12.01	12.01	10.86
Ash in Feed, dry wt. %	20.46	20.46	18.68
Yields, wt. % maf			
Gas	20.55	14.47	16.77
Tar	11.06	13.40	11.37
Char	57.56	*(69.00) 60.91	60.63
Water	11.02	11.17	10.95
Total Recovery	100.19	*(108.09) 100.00	99.72
Yields of Gases, wt. % maf			
H_2	1.58	0.07	0.15
CO	3.74	4.06	6.70
CO_2	11.43	8.70	7.84
CH_4	1.61	1.33	1.70
C_2H_4	0.24	0.10	0.15
C_2H_6	0.18	0.12	0.11
C_3	1.40	0.06	0.06
C_4	0.37	0.04	0.06
BTX	N.D.	N.D.	N.D.

N.D. Not Determined
* Char corrected for sand blown from bed, value in brackets is measured amount.

Table 29

Particle Size Distribution
Pilot Plant Runs No. 55, No. 64 and No. 65

Size Range		Saskatchewan (Coronach) Lignite				Highvale Subbituminous	
		Run No.55		Run No.65		Run No.64	
Mesh.	µm	wt. Percent	cumm. wt. Percent	wt. Percent	cumm. wt. Percent	wt. Percent	cumm. wt. Percent
+12	+1680	0.28	0.28			0	0
-12 +20	-1680 +840	5.72	6.00	9	9		
-20 +30	-840 +590	17.70	23.70			18	18
-30 +60	-590 +250	35.60	59.30	43	52	45	63
-60 +100	-250 +149	10.91	70.21				
-100 +200	-149 +74	11.02	81.23	20	72	28	91
-200 +325	-74 +44	4.81	86.04				
-325	-44	13.52	99.56	28	100	9	100

those of bench scale Run 178 shows that the pilot plant produced more char and tar and less gas than the bench scale run, possibly because of differences in the char pot temperatures in the two units. The pilot plant char pot was neither heated nor insulated and therefore the separated char quickly cooled well below the run temperature. The ultimate analysis of the chars, presented in Table 30, shows that pilot plant chars had higher hydrogen, nitrogen and oxygen contents and lower carbon contents than bench scale char, suggesting that bench scale char had undergone greater devolatilization than pilot plant chars and had therefore yielded more gaseous products. Contrary to gas yields however, tar yields were higher for pilot plant runs than for bench scale runs. Presumably the slow char devolatilization in the hot char pot preferentially yielded gaseous products as opposed to liquid products. These observations parallel those for increasing vapour residence times as reported by Scott (1984). It was reported that increasing the vapour residence time reduced char and tar yields while increasing the gas yields. It is possible that a hot cyclone and char pot will affect the pyrolysis reactions in the same way that a longer vapour residence time does. Table 28also shows that the H_2 and C_3 gas yields for the bench scale run are higher than would be predicted by previous results for Estevan lignite pyrolyzed at 650° C or by results reported by Scott (1984) at 600° C. On the other hand pilot plant yields of H_2 , C_3 and C_4 gases are unusually low. It is possible that the larger particle sizes fed to the pilot plant in Run P-55 introduced some mass and/or heat transfer limitations which hindered the release of specific product species. Also,

recirculation of product gases could affect individual product yields. Pilot plant Run P-65 was done at a higher temperature (647°C vs. 587°C) and with smaller particle (326 μm vs. 495 μm average) than pilot plant Run P-55. Results in Table 28 show that the higher temperature and smaller particle sizes in the pilot plant resulted in about 2 percent more gas being produced at the expense of the tar yield. Char and water yields were about the same for both runs. Yields of individual gas components show that pilot plant runs produced less H_2, CO_2 and C_2+ hydrocarbons and more CO which suggests that the recycling of the gas products resulted in promotion of the water-gas shift reaction and secondary cracking of the hydrocarbon gases.

Table 30 presents the ultimate analyses and elemental balances of pyrolysis products for Runs P-55 and 178. The ultimate analyses of the two tars collected from Run P-55 are similar to each other. The char ash values in brackets represent the ash content of the entire char sample based on a 100 percent ash balance. The other char ash values were used only to calculate the ash-free elemental analysis of the micro analytical sample.

It is apparent from the results of Table 30 that the char and the tar produced in the pilot plant showed a somewhat higher H/C ratio than did that obtained from the bench scale unit. The product gas from the pilot plant was much lower in H_2 and CH_4, which might partially explain this difference.

The poor ash balances led to an adjustment of ash content in

Table 30

Bench Scale and Pilot Plant Runs Using Saskatchewan (Coronach) Lignite

Ultimate Analysis and Elemental Balance of Pyrolysis Products

		Run 178 Bench Scale Unit	Run P-55 Pilot Plant Unit
Feed as is, (maf)	C	48.89 (55.56)	48.89 (55.56)
	H	3.87 (4.40)	3.87 (4.40)
	N	0.71 (0.81)	0.71 (0.81)
	O	(39.23)	(39.23)
	Ash	15.84 (20.46) dry	15.84 (20.46) dry
	H_2O	12.01	12.01
	H/C	0.95	0.95
Tar (dry)	C	74.59	42.01 (67.98) 32% from Schrader bellows; 66.69 68% washed from condensers
	H	7.07	9.26 (8.02); 7.00
	N	1.20	1.17 (1.95); 1.42
	O	17.14	(20.05); 24.89
	H_2O	0	39.97; 0
	H/C	1.14	(1.38); 1.26
Char as is, (maf)	C	69.75 (89.32)	53.25 (72.42) 2.5% from filter paper; 54.42 (80.23) 97.5% from char pot
	H	1.86 (2.38)	2.41 (3.28); 1.89 (2.79)
	N	0.48 (0.61)	0.77 (1.05); 0.53 (0.78)
	O	(7.69)	(23.25); (16.20)
	Ash	21.91 (27.61)	26.47 (24.14); 32.17
	H/C	0.32	0.54; 0.42
Gas	C	37.98	37.09
	H	11.24	3.12
	O	50.78	59.79
C Balance		98.92	93.7
H Balance		153.33	102.1
O Balance		65.92	80.9
Ash Balance		79.33 (100)	133.3 (100)

Ash values in brackets have been adjusted for 100% ash balance.

Other ash values are for microanalytical samples only and are not necessarily representative of the whole.

the chars to 100%. These values were then used in calculating the maf values (shown in brackets) for the chars. With this adjustment, C balances were satisfactory, as was the pilot plant H balance. The H balance for the bench scale unit, together with the high H yield, suggests that some hydrogen contamination of the unit from earlier hydrogasification tests might have occurred.

The operation of the pilot plant with a lignite feed did not present any problems. The run continued until the feed supply in the hopper was exhausted. The feed rate was 1.45 kg/h in Run P-55 and 1.36 kg/h in Run P-65 and was kept as low as possible to maintain the temperature above 580°C. Feeding the coal did not present any problems and the pressure drop across the reactor remained constant which suggested that char accumulation in the fluid bed was minimal. A potential problem area was indicated by an increasing pressure drop across the cold condenser. The hot condenser temperature was lowered from 60° to 20°C in order to condense more tar in this condenser and thus reduce the plugging of the second ice-water condenser. The condenser tubes were washed with a mixture of methanol, methylene chloride and tetrahydrofuran and the solvent was evaporated to recover about 46 to 68 percent of the tar product. Another 22 percent of the tar was recovered in the separators. The remainder was collected in the cotton-wool filter and in the condensate bottles. Water was measured in the condensate bottles and in the condenser washings and gas sample. Char was collected in the char pot and by filtering the condenser washings. A sample of gas was taken

after 90 minutes run time and analyzed by gas chromatography.

Table 31 shows results from the pyrolysis of Highvale sub-bituminous coal using the pilot plant unit and the bench scale unit. The bench scale runs were done in 1982 when the apparatus and procedures differed somewhat. The smaller reactor was used without a cyclone and water content was determined by taking a hot vapour sample and analyzing this in a Carle gas chromatograph. Table 31 shows that the pilot plant unit yielded more gas and water and less tar and char than the bench scale unit. It is probable that inaccurate water determinations for the bench scale runs, which was a greater source of error in 1982 than in the present work, resulted in underestimated water yields and overestimated tar yields. In the pilot plant unit the recycling of the product gas may also have affected the final yield of products. The pilot plant unit produced 3 percent more CO than the bench unit. High CO and water yields suggest that the water-gas shift reaction was proceeding to a greater extent. Methane yields were slightly higher (1.5% vs. 1.1%) and C_2 and C_3 hydrocarbons were slightly lower (0.36% vs. 0.76%) for the pilot plant run compared to the bench scale runs. Recycling of the higher uncondensable hydrocarbons such as C_2 to C_4's and BTX's may have promoted secondary cracking reactions, resulting in decreased yields of these products and increased yields of lighter hydrocarbons such as methane. The pilot plant runs had a much wider feed particle size distribution than the bench scale runs, as shown in Table 29. The average Highvale coal particle size used in the pilot plant run (442 μm) was larger than that

Table 31

Pyrolysis of Highvale Subbituminous Coal

Comparison of Bench Scale Unit and Pilot Plant Unit

Run No. Feed	47 (Nov. 1982) Bench Scale N_2 atm	22 (March 1982) Bench Scale N_2 atm	64 (June 1985) Pilot Plant N_2+recirculated gas
Temperature, °C	650	650	642
Coal Size, µm	-149 +74	-149 +74	-1680
Sand Size, µm	-250 +149	-250 +149	-840 +590
Sand Amount, gms	15.0	15.0	2100
Duration of Run, min.	36	21	126
Wt. of Coal Fed, gms	8.34	13.9	2820 (1.34 kg/hr)
Vapour Residence Time, secs.	0.44	0.44	0.44
Moisture in Feed, wt. %	17.3	17.3	9.58
Ash in Feed, dry wt. %	10.7	10.7	12.17
Yields, wt. % maf			
Gas	16.23	14.1	17.12
Tar	10.4	11.2	7.23
Char	69.1	66.5	64.45
Water	4.2	2.7	11.85
Total Recovery	99.93	94.4	100.65
Yields of Gases, wt. % maf			
H_2	0.28	0.19	0.13
CO	3.90	3.94	6.81
CO_2	9.72	8.22	8.15
CH_4	1.09	1.03	1.49
C_2H_4	0.26	0.28	0.15
C_2H_6	0.19	0.22	0.14
C_3	0.35	0.22	0.07
C_4	N.D.	N.D.	0.19
BTX	0.43	N.D.	N.D.

N.D. Not Determined

used in the bench scale run (112 μm). However during both bench and pilot plant runs the char accumulation in the reactor was negligible. The coal used in the pilot plant run had aged for approximately three years following the bench scale runs, and the effect of this aging on tar yields is unknown at present.

Pilot Plant Run P-56 operated with a highly caking Devco bituminous coal sample. Reactor temperature was maintained at an average of 675°C. Upon start-up the pressure drop across the separators increased dramatically causing operating problems. A high pressure in the hopper blew some coal past the twin screws and plugged the reactor feeder tube. After 22 minutes the run was stopped and the plugged tubes cleared. The mist separators and associated tubing contained a small amount of a sticky char-like solid which had apparently built up in small sections of the tubing causing the high pressure drop. The tubing was shortened and both separators were connected in series between the two condensers. The temperature of the hot condenser was maintained at about 23°C. The run was started again and the pressure drop across both condensers and the cotton-wool filter increased steadily. Surprisingly, after 32 minutes total run time of maintaining a steady pressure drop across the reactor, the bed suddenly plugged, and the run was stopped. Inspection of the reactor showed a high degree of agglomeration in the sand bed. Presumably this agglomeration of the sand progressed steadily during the run causing channeling and poor fluidization behaviour. Further tests indicated that the porous plate distributor was also badly plugged either due to deterioration

of the porous properties of the metal or to plugging by the plastic behaviour of the caking coal. The latter cause seems to be indicated since oxidation at 700°C cleared the restricted flow through the plate. The rise in pressure drop across the condensers was not caused by the plugging of the condensers themselves but by the plugging of the two separators between the condensers. A brown, solid, char-like product was observed in the separators stuck to the walls near the entrance and exit ports thus restricting the gas flow. The majority of this product was found to be soluble in tetrahydrofuran (THF). The ultimate analysis of Devco coal and its pyrolysis products are given in Table 32. The analysis of this solid product from the separators and its THF soluble fraction were quite similar and resemble that of a tar product. Since it was totally combustible at 950°C it was probably a volatile product at the reaction temperature. Upon cooling it became a sticky condensed substance adhering to surfaces in its path. Observation of the char recovered in the char pot revealed that the particle size of this product was larger than the particle size of the original coal fed, suggesting that agglomeration can occur to a limited extent without upsetting the operation of the process. Agglomerated char particles were not large enough to block any passages in the system.

Forestburg sub-bituminous coal was fed in Pilot Plant Run P-57. Both mist separators were located between the two condensers as in Pilot Plant Run P-56. The average temperature of the fluid bed was 683°C. As for the Devco, the pressure drop

Table 32

Devco Bituminous Coal

Ultimate Analysis of Pyrolysis Products from Pilot Plant Run #56

weight percent as is, (maf)

	C	H	N	O (by diff)	Ash	H/C
Devco Bituminous Coal (0% H_2O)	82.38 (85.35)	5.27 (5.46)	2.38 (2.47)	(6.72)	3.48	.77
Char from Char Pot	79.78 (88.11)	1.66 (1.83)	1.06 (1.17)	(8.89)	9.45	.25
Solids from Separators	84.81	6.25	0.92	8.02	0	.88
Tar Solvent extracted from Separators Solids	83.34	6.84	1.38	8.44	0	.99

across both the cold condenser and the cotton-wool filter increased substantially. In only ten minutes at a low (1.5 kg/h) feed rate, the pressure drop across the cold condenser increased from 20" H O to over 100" H O while the drop across the cotton-wool filter increased from 35" to 65" H O. Because of these problems the run had to be stopped after only 14 minutes of operation. Inspection of the recovery system revealed that most areas were fairly clean and free of blockages. There was some product build-up in the separator inlet tube which may have been responsible for the high pressure drop across the second condenser. It is possible that once a build-up of the heavy and sticky tar product begins a "snowball" effect occurs which results in an accumulation of the product in a small area, causing a flow restriction. The cotton-wool filter did not appear to be heavily plugged as its differential pressure indicator suggested. It is possible that the method of packing the filter contributed to the pressure drop across it.

It can be concluded from these tests that if coal is to be routinely pyrolyzed in the pilot plant unit, some improvements to the product recovery system will be necessary. The major problem during these initial runs was the plugging of the mist separators and their associated tubing. However, incomplete collection of the liquid products in the condensers necessitated the use of these separators. A possible replacement for this recovery system would involve the use of an electrostatic precipitator or a liquid scrubber which would separate the liquid products, including the tar fog, from the gas stream.

On the basis of the runs with lignite, which yielded acceptable quantitative data, it appears that the larger unit using a recycle gas tends to produce at least as high a yield of tar as the bench scale unit. Some difference in gas product distribution occurs with the larger unit, giving a gas which does not appear to be as much influenced by the shift reaction as that in the bench scale unit. Because of the highly endothermic nature of coal pyrolysis reactions and the high temperature required, lower feed rates per unit of fluid bed volume must be used in order to achieve an adequate rate of heat transfer to the coal particles.

vii) Controlling the Agglomeration of Caking Coals in a Fluidized Bed

(a) Pre-Oxidation of Coal

Several attempts were made to control the agglomeration of the fluid bed when caking bituminous coals were pyrolyzed. It is known that surface oxidation of the coal will reduce or eliminate the caking properties of the coal but will also reduce the yield of pyrolytic tar. To reduce the caking properties which result in agglomeration of the fluid bed but to maintain maximum liquid yields was the goal of the first set of tests.

Table 33 presents data from three runs with the heavily caking Devco bituminous coal. Runs 106 and 142 have been previously reported by Scott (1984) in determining the effect of

Table 33

Pyrolysis of Devco Bituminous Coal

Run No.	106	142	183
Feed	raw	oxidized*	raw
atm	N_2	N_2	Air : N_2 (6.6% O_2)
F.S.I.	7.5	0	7.5
Temperature, °C	650	650	650
Coal Size, μm	-149 +74	-149 +74	-250 +74
Sand Size, μm	-590 +250	-590 +250	-590 +300
Sand Amount, gms	22.59	22.6	60
Duration of Run, min.	18	14	15.66
Wt. of Coal Fed, gms	9.89	13.87	18.69
Vapour Residence Time, secs.	0.8	0.8	0.62
Moisture in Feed, wt. %	0	0	0
Ash in Feed, dry wt. %	2.8	2.8	3.48
Yields, wt. % maf			
Gas	6.2	7.7	31.94
Tar	16.6	12.8	9.09
Char	67.8	67.1	42.18
Water	4.7	4.9	13.47
Total Recovery	95.3	92.5	96.68
Yields of Gases, wt. % maf			
H_2	0.1	0.17	0.45
CO	0.7	1.80	11.98
CO_2	1.2	2.45	15.63
CH_4	1.5	1.88	2.10
C_2H_4	0.2	0.25	0.33
C_2H_6	0.4	0.38	0.38
C_3	0.4	0.33	0.38
C_4+	1.2	0.30	0.61
BTX	0.6	0.10	0.06

* Oxidized in Air at 105°C for 27 days

pre-oxidation on pyrolysis of caking coals. The coal feed for Run 142 was held at 105°C for 27 days prior to pyrolysis. The major result of this pretreatment was a reduction in the free swelling index of the coal from 7.5 to 0 and a subsequent elimination of the agglomeration problem on pyrolysis, accompanied by an approximate 25 percent loss of pyrolytic tar yield. For our tests, another sample of Devco coal was pre-oxidized in air at 90°C for 2 hours. The free swelling index of the coal was not determined, however, an attempt to pyrolyze the sample failed due to plugging of the reactor injection tube. Apparently, a sufficient reduction of the caking properties did not occur. A minimum level of pre-oxidation may exist for which the swelling properties of the coal have been sufficiently reduced to prevent agglomeration, but which will not significantly reduce the pyrolysis tar yield. This possibility requires further study.

Table 33 also shows results from Run 183 in which air (about 30% of the total gas flow) was used instead of nitrogen to convey the coal particles from the feeder to the reactor. The pyrolysis atmosphere, therefore, consisted of 6.6 percent O_2 and 93.4 percent inert nitrogen. The use of the air stream in the feeder allowed the coal to reach the fluid bed without plugging the injection tube. Once in the fluid bed however, the sand and char particles formed agglomerates and eventually plugged the reactor. The agglomeration problem was therefore not sufficiently improved by adding oxygen to the pyrolysis atmosphere. Table 33 also shows that the tar yield was reduced

by approximately 45 percent. Char yields were also decreased while gas and water yields increased. Much of the coal was essentially combusted, resulting in high yields of carbon oxides.

Another attempt at controlling the agglomeration problem was made by replacing the sand in the bed with limestone. The Devco coal was fed with some difficulty, but after the run large chunks of coke were discovered in the bed which would have eventually plugged the reactor. No pyrolysis products were collected. The conclusion was reached that the addition of limestone did not prevent the agglomeration of the fluid bed by caking coal, contrary to a recent report.

Pyrolysis of a pre-oxidized Forestburg sample was done also to determine any effects of aging on this sub-bituminous coal. The pre-oxidized coal was held at 110° C for two hours to promote surface oxidation of the coal. Subsequent pyrolysis yielded results reported in Table 34 which are very similar to those of the untreated coal. Tar yields remained unchanged for the two coals while the pre-oxidized coal produced 2 percent less gas and 1 percent less water than the untreated coal. There is the possibility that the raw coal of Run 179 had also undergone some surface oxidation by exposure to air, although the coal was stored in sealed containers before use. To determine the effects of aging, a coal pre-oxidized at known conditions must be compared to one which has been very carefully collected, and stored under inert gas. However, given the normal techniques used in coal processing, it is doubtful if there exists any such material as a "fresh" coal, and some degree of surface oxidation

Table 34

Pyrolysis of Forestburg Subbituminous Coal #2
Pre-Oxidized in Air for 2 hours at 110 C

Run No.	179	192
Feed	raw	oxidized
Temperature, °C	650	650
Coal Size, μm	-250 +62	-250 +62
Sand Size, μm	-590 +300	-590 +250
Sand Amount, gms	60	60
Duration of Run, min.	25	30
Wt. of Coal Fed, gms	63.25	73.83
Vapour Residence Time, secs.	0.62	0.62
Moisture in Feed, wt. %	4.33	1.69
Ash in Feed, dry wt. %	6.45	6.45
Yields, wt. % maf		
Gas	21.73	19.92
Tar	10.69	10.48
Char	54.61	58.14
Water	12.46	11.46
Total Recovery	99.49	100.00
Yields of Gases, wt. % maf		
H_2	0.90	1.02
CO	7.45	5.87
CO_2	8.04	7.64
CH_4	2.38	3.45
C_2H_4	0.90	0.53
C_2H_6	0.28	0.26
C_3	0.69	0.47
C_4	0.94	0.51
BTX	0.15	0.18

is unavoidable. However, this degree of surface oxidation is not sufficient to affect pyrolytic tar yields for either sub-bituminous or bituminous caking coals, and it does not affect the agglomeration tendencies of caking coals.

(b) **Blends of Caking and Non-Caking Coal**

The difficulty in determining the optimal degree of pre-oxidation of a caking coal led to the concept that agglomeration tendencies might be controlled to some degree, by using a blend of non-caking sub-bituminous coal and a strongly caking bituminous coal. Accordingly, a number of mixtures of Forestburg sub-bituminous (#1) and Balmer low volatile bituminous coal were made up, and the free swelling indices determined. Results are shown in Table 35, and indicate that for these two coals the FSI is more or less directly proportional to the amount of caking coal in the blend. On this basis, it was decided to attempt the pyrolysis of a 50/50 mixture by weight of the two coals.

The major operating problem encountered with a caking coal is due to its sticky plastic state at pyrolysis temperatures which causes plugging of the coal injection tube and agglomeration of the sand in the fluid bed reactor. The Balmer and Forestburg coal samples used were received from E.M.R. in 1982 (Balmer #1 and Forestburg #1).

Tables 2 and 3 show the analyses of the Balmer and Forestburg coals by various sources as well as the analysis of

Table 35

Blends of Forestburg and Balmer Coals - Free Swelling Index

Coal Mixture, ratio by weight	FSI* (4 results)
Forestburg, 100%	0, 0, 0, 0
Balmer/Forestburg 1:3	1, 0, 0, 0
Balmer/Forestburg 1:2	1, 1½, 1, 1
Balmer/Forestburg 1:1	2, 2, 1½, 1½
Balmer/Forestburg 2:1	2, 2, 2½, 2½
Balmer/Forestburg 3:1	3, 3, 3, 3
Balmer, 100%	3½, 4, 4, 4½

*Tests performed by A. Newman, Coal Research Laboratory, University of Waterloo

the Balmer-Forestburg coal blend. Although some variation between the values exist (i.e. Forestburg by REMS68.93% Cvs. Forestburg by U.B.C. 76.4% C), on a moisture and ash-free basis a reasonable agreement is obtained. Measured values from the analysis of the coal mixture represent the approximate calculated averages of values from the two individual coals.

Table 36 gives results of four pyrolysis runs using the Balmer-Forestburg coal mixture (Runs 152, 154, 155, 157) as well as the results of two previous runs (Runs 133 and 111) with the individual coals under comparable conditions. Although the free-swelling index of the coal mixture is given as 2 compared with 4 for Balmer and 0 for Forestburg coal, operating problems were still experienced during a pyrolysis run. The coal injection tube plugged from two to ten times during a 30 minute run.

Agglomeration of char and sand in the fluid bed reactor restricted gas flow through the system and resulted in high pressure drops (about 60" H_2O). Variation of the operating parameters (temperature, residence time, sand size) did not improve the performance of the coal mixture. During all the runs the formation of a high porosity coke agglomerate caused plugging in various locations of the apparatus. This spongy material plugged the free space at the top of the reactor during Run 152 resulting in about 85 percent of the char remaining in the reactor. The higher temperature (700°C) of Run 154 produced more gaseous products (10.65% vs. 7.71%) but had no significant effect on the plugging problem. Runs 155 and 157 were done at 650°C for

Table 36

Pyrolysis of Balmer-Forestburg Coal Mixture, 50/50 (June 1984)

Moisture: 3.06% Ash: 8.59% mf

Run No.	152	154	155	157	133*	111**
Temperature, °C	555	700	650	650	650	650
Coal Size, μm	-250+ 74	-250+ 74	-250+ 74	-250+ 74	-149+ 74	-149+ 74
Sand Size, μm	-590+250	-590+250	-300+250	-840+590	-250+149	-840+590
Sand Amount, gms	60	60	60	90	25	
Duration of Run, min	35	27	32	30	30	22.6
Wt. of Coal fed, gms	37.98	40.14	45.48	41.64	13.94	6.29
Vapour Residence time, secs	0.56	0.56	1.00	0.30	0.45	0.45
Moisture in Feed, %	3.06	3.06	3.06	3.06	10.00	0.78
Ash in Feed, % dry	8.59	8.59	8.59	8.59	7.48	8.84
Yields, wt.%, maf						
Gas	8·70	12·02	9·12	7.64	19.17	5·90
Tar	7.61	7.22	6.27	6.07	9.74	10.70
Char	71.27	69.55	75.94	73.54	58.58	76.78
Water	≈4.06	6.05	6.75	4.40	4.67	4.56
Total Recovery	91.64	94.84	98.08	91.65	92.16	97.94
Yields of Gases, % maf by wt.						
H_2	0.17	0.37	0.15	0.35	0.35	0.40
CO	1.81	2.79	1.83	1.95	5.49	0.80
CO_2	4.11	5.55	4.63	3.39	10.66	1.80
CH_4	1.48	1.97	1.42	1.35	1.50	1.19
C_2H_4	0.19	0.30	0.14	0.14	0.32	0.10
C_2H_6	0.29	0.32	0.28	0.19	0.23	0.30
C_3	0.24	0.29	0.23	0.14	0.31	0.20
C_4+	0.41	0.43	0.46	0.13	0.29	1.1

* Forestburg sub-bituminous #1
** Balmer low volatile bituminous #1

1.00 and 0.30 second residence times respectively. Run 155 experienced some plugging of the cyclone with less plugging of the reactor than in previous runs. Almost 65 percent of the char produced remained in the reactor with 18 percent blowing over into the condensers and the remainder either in the char pot or in the cyclone. With the higher gas flow rates (7.5 ℓ/min) larger sand sizes (-840 + 590 μm) and more sand (90 gms) in Run 157, 55 percent of the char produced remained in the reactor, 18 percent blew into the condensers and 27 percent formed a plug in the cyclone or entered the char pot. The values in Table 36 indicate that tar yields for the blend were greatest at 555°C with a 0.555 second vapour residence time and a 92.6 percent recovery. These tar yields are lower than those reported previously for the individual coals (6.74% vs. 8.12 and 10.67%).

In conclusion, mixing a non-caking coal with a caking coal delayed the plugging of the injection tube and fluid bed reactor allowing more coal to be fed before the run had to be stopped. However, plugging still occurred which indicated that the fluid bed reactor may not be the best design for the pyrolysis of caking coals, even when mixed with a non-caking coal unless the blend contains a majority of the non-caking coal. In Australia, the CSIRO pyrolysis process pyrolyzes caking coals successfully in a fluidized bed reactor. However, no coal with an FSI over 3.5 has been tested, and these were not strongly caking coals. In addition, the CSIRO reactor runs at considerably higher gas velocities than does the Waterloo unit, and has recently been found to be operating at the borderline

between fluidized bed and spouted bed behaviour. (The pilot size unit, 20 kg/hr feed rate, has a conical inlet and no distributor plate, so that spouting operation is possible - Private Communication 1985). In general, it has been found by Watkinson in his gasification and pyrolysis studies (e.g. Al-Jarallah, 1983) that spouted bed operation is feasible with caking coals.

viii) **Pyrolysis of Caking Coals**

Two investigations were carried out to attempt to resolve some uncertainties arising from earlier work concerning the tar yields obtainable from a caking coal (Balmer #1) in a CO_2 atmosphere, and concerning a very high tar yield reported for Sukunka bituminous coal (Al-Jarallah, 1983). Proximate and ultimate analyses of these coals were given in Tables 6A and 6B.

A major operating problem was encountered due to the strongly caking nature of Balmer coal which caused agglomeration of the sand in the small fluid bed reactor after a relatively short operating period. However, one run was completed, with considerable difficulty, in a CO_2 atmosphere, both to obtain a liquid product sample and to check the effect of a CO_2 atmosphere on liquid yields, inasmuch as previous results were inconclusive. The data for this test (Run 151) are summarized in Table 37. The coal was conditioned prior to the test by being exposed to a flow of CO_2 for two hours. As can be seen from the results given in Table 37, compared to other runs also at 650°C which are summarized in Table 38 from earlier work, a coal which has been

Table 37

Run No. 151

Pyrolysis of Balmer Coal in Carbon Dioxide Atmosphere

Feed -250 + 74 μm, 0.8% moisture, 8.8% ash
26 mm Diameter Reactor with hot cyclone, 50 gms Ottawa sand -30 + 60

Coal Fed 14.91 gm., Temperature 650°C

Yields, % as Fed		% maf
Tar	8.05	8.94
Char	75.12	73.66
Gas	7.78	8.64
Water	N.D.	N.D.
Light Org.	N.D.	N.D.
Total	90.95	91.24
H_2	0.48	
CO	3.23	
CH_4	2.85	
C_2H_4	0.31	
C_2H_6	0.48	
C_3	0.27	
C_4	0.16	
CO_2	N.D.	

Table 38

Summary of Pyrolysis of Balmer Coal at 650°C

Effect of Reaction Atmosphere

Feed is -149 + 74 μm, 0.8% moisture, 8.8% ash

Run No.	Residence Time secs.	Tar Yield % as fed	Total Recovery % as Fed	Atmosphere
110	1.4	8.3	97.6	N_2
111	0.45	9.70	98.4	N_2
112	0.80	6.11	84.6	H_2
113*	0.80	22.16	144.5	CO_2
115*	0.80	18.71	122.1	CO_2
116	0.80	5.60	95.7	N_2
117	0.80	13.22	113.4	CO_2
118*	0.80	11.77	100.9	CO_2
123*	0.80	8.85	97.1	CO_2
125*	0.80	7.23	98.7	CO_2
151	0.45	8.05	91 to 95	CO_2

*Runs given in Progress Report 9, August, 1983. For these runs, tar yields were calculated as a % of total recovery. Because of errors due to adsorption of CO_2, these yields are probably high.

fully aged in CO_2 does not appear to give any increase in tar yield over that obtained in an N_2 atmosphere. It is still possible that fresh coal fed with N_2 but with CO_2 as the fluidizing gas might show some improved tar yield but this is not likely to be the case, particularly in view of pilot plant results with sub-bituminous coals in an $N_2/CO/CO_2$ atmosphere, which showed little effect on tar yields.

During April, 1984, tests with Sukunka coal were completed, to the best of our ability. Sukunka coal had the most difficult caking properties of any of the bituminous coals tested. As a result runs were relatively short and of variable length, depending on the severity of the caking and agglomeration in the fluid bed. A summary of the results with the Sukunka coal is given in Table 39. The highest tar yield obtained was obtained in a CO_2 atmosphere, but it was only slightly higher than that obtained in an N_2 atmosphere. Also, during the CO_2 run, feed was stopped periodically and air admitted to burn off accumulated char, so the char inventory never built up in this run (150) as it did for the other runs (143-146).

In summary, the fluidized bed reactor does not appear to be ideal for pyrolysis of caking coals. Either the coal must be modified in properties e.g. pre-oxidation with some probable loss of tar yield, or a reactor designed specifically for this type of coal should be used. Further, the use of different reaction atmospheres, and in particular, N_2 or CO_2, appears to have little effect on either tar yields or on agglomeration properties at temperatures below about 700°C.

Table 39

Pyrolysis of Sukunka Coal (April, 1984)

Moisture 1.9% Ash 9.0%, N_2 atmosphere

Run No.	143	144*	145*	146*	150**
Temperature, °C	533	650	680	666	650
Coal Size, µm	-250 + 74	-250 + 74	-149 + 74	-149 + 74	-250 + 74
Sand Size, µm	-595 + 250	-595 + 250	-595 + 250	-841 + 595	-595 + 250
Sand Amount, gms	60	60	25	100	60
Duration of Run, min	30	42	21	15	31
Wt. of Coal Fed, gms.	42.4	21.6	13.9	11.8	8.7
Vapour Residence Time, s	0.50	0.50	0.50	0.35	0.50
Yields, % as Fed					
Gas	2.94	5.02	5.07	4.02	7.23
Tar	4.29	9.73	12.16	7.88	13.22
Char	91.75	N.D.	79.21	77.97	N.D.
Water	1.63	1.29	N.D.	N.D.	N.D.
Total Recovery	100.6	-	96.4	89.9	-
Yields of Gases, % as Fed by wt.					
H_2	0.08	0.32	0.27	0.41	0.23
CO	0.26	0.46	0.65	0.41	3.49
CO_2	1.22	1.25	0.83	0.76	-
CH_4	0.82	1.84	2.27	1.72	2.37
C_2H_4	0.07	0.18	0.20	0.15	0.29
C_2H_6	0.21	0.32	0.40	0.34	0.39
C_3	0.16	0.23	0.26	0.20	0.22
C_4+	0.14	0.42	0.20	0.19	0.24

*Severe agglomeration and char accumulation in the reactor

**CO_2 atmosphere. During this run, about every five minutes the feed was stopped and after disconnecting gas collection bag and feeder, air was admitted to burn off char accumulated in the bed.

Runs 147, 148, 149 were unsuccessful due to high rate of agglomeration.

ix) Reactivity of Coals and Chars

Several raw and acid washed coals have been characterized by thermogravimetric analysis in nitrogen and carbon dioxide. Tables 5 and 15 show the proximate analysis of these coals as well as the proximate analysis of two pyrolysis chars. The important conclusion from this data was that acid washing of Estevan lignite did not alter the volatile or fixed carbon content of the coal. It was also observed that char yields from pyrolysis of the lignite and sub-bituminous coals were between 2 and 4 percent greater than the corresponding fixed carbon content of the feed on an maf basis.

The effect of the rank and cation content of the coal on the char reactivity in carbon dioxide was also studied using thermogravimetric analysis. Figure 17 shows the weight loss - temperature history of Forestburg coal in carbon dioxide, which is very similar to Figure 18 which shows the weight loss - temperature history of Estevanan lignite in carbon dioxide. However, for both coals, a high percentage of the fixed carbon reacts in CO_2 at less than 950° C. To properly compare char reactivities, the coal should first be devolatilized in nitrogen before introducing carbon dioxide at a constant temperature. Figure 19 shows the results of four separate TGA runs on Estevan lignite #4 given different cation removal pretreatments but with identical devolatilization steps which conform to the TGA proximate analysis method. The results of Figure 19 clearly illustrate the differing char reactivities for different coal

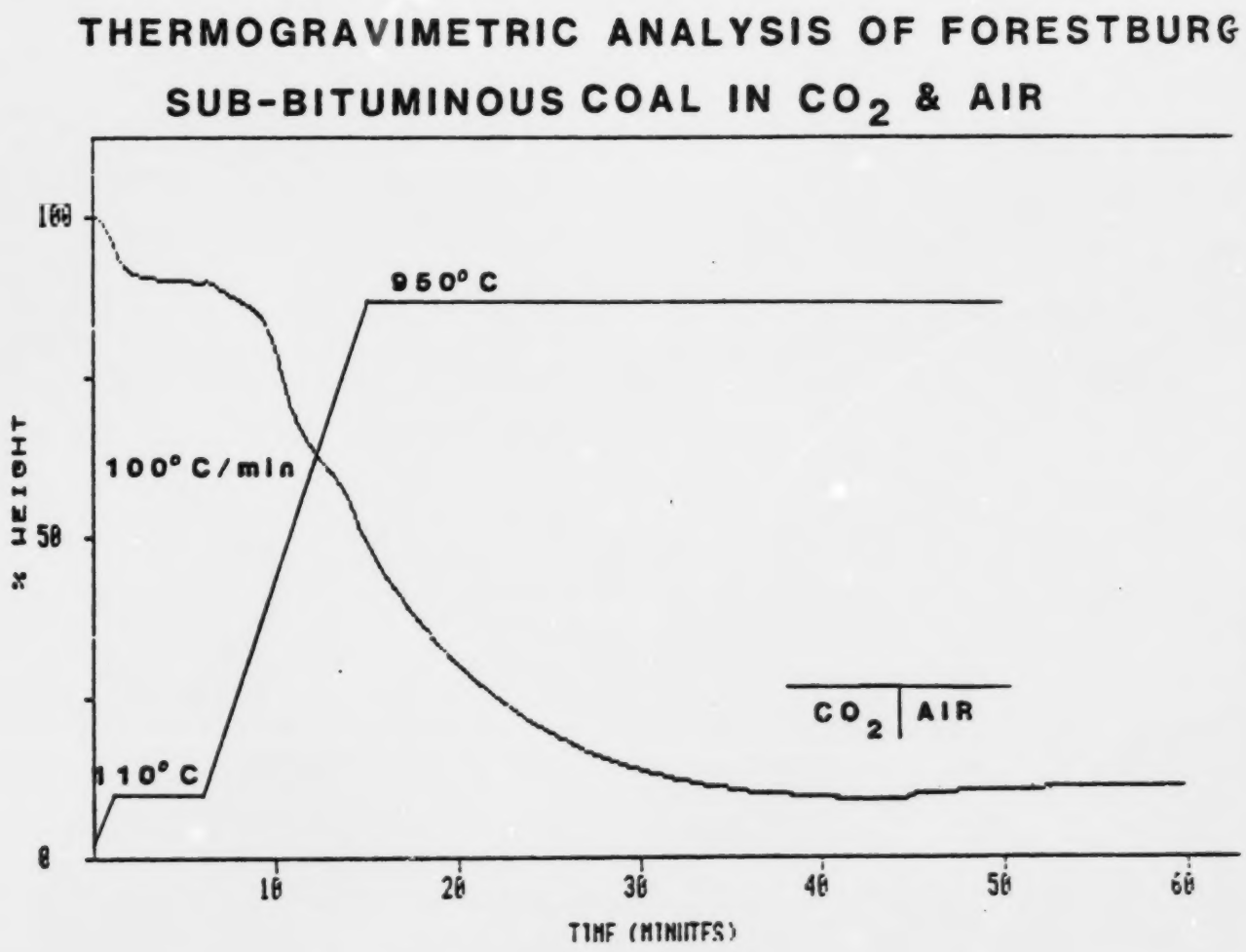

Figure 17 Thermogravimetric Analysis of Forestburg Sub-Bituminous Coal #2 in CO_2 and Air

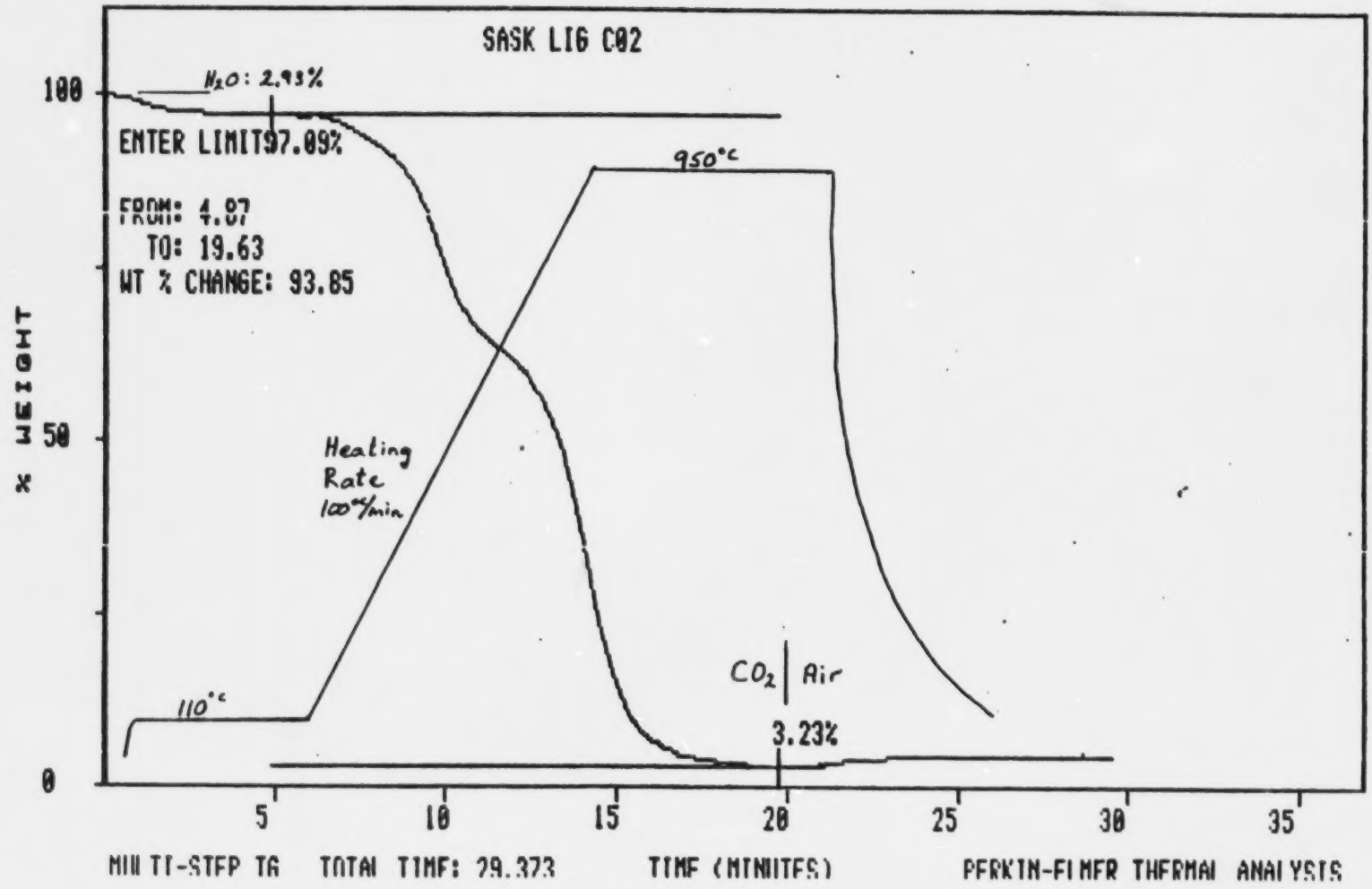

Figure 18 Thermogram of Estevan Lignite Coal #4 in CO_2

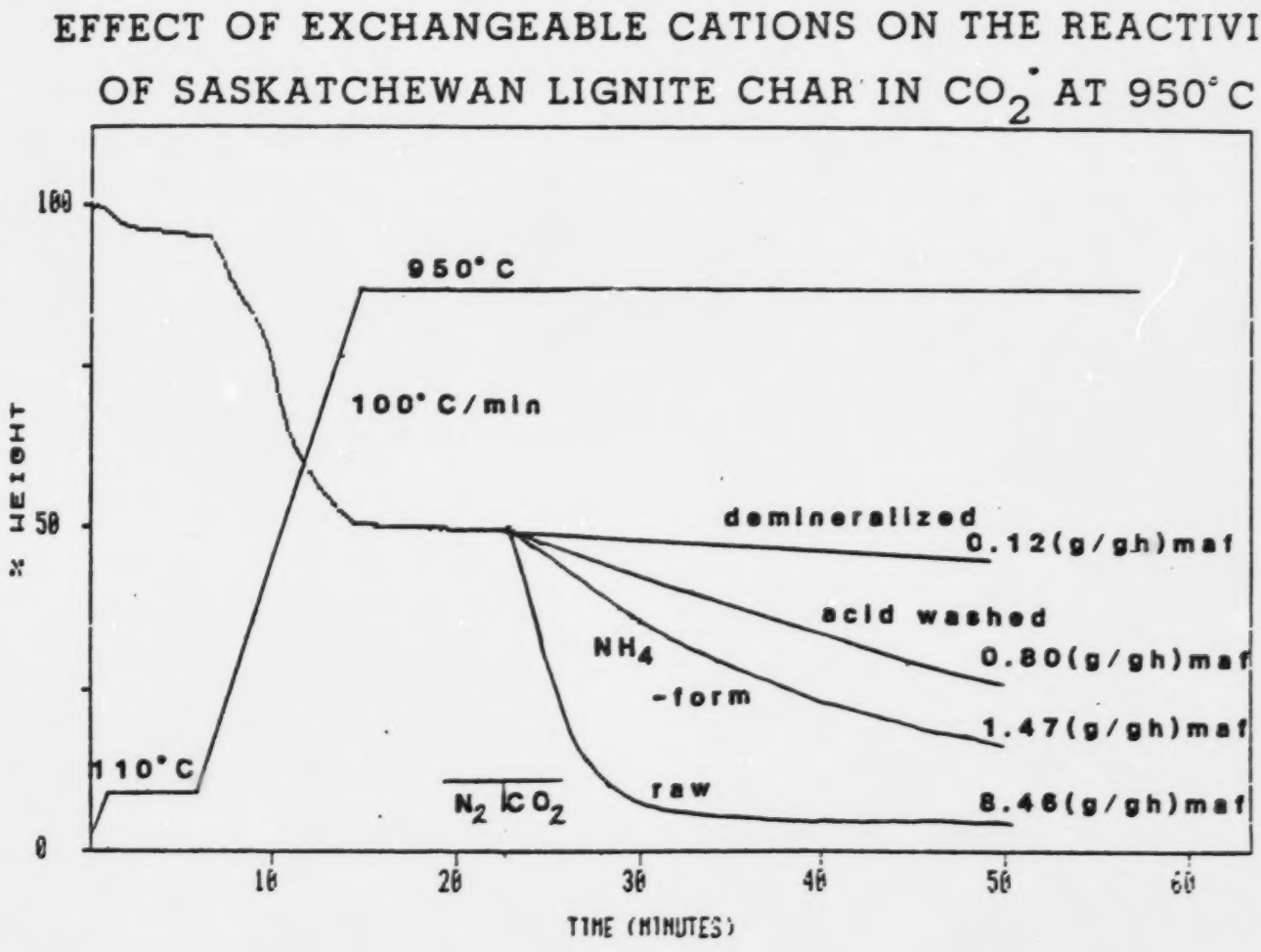

Figure 19 Effect of Exchangeable Cation Content on the Reactivity of Estevan Lignite Char in CO_2 at 950°C

treatment. The numerical values given in Figure 19 are the initial rates of reaction of the Estevan lignite chars in carbon dioxide at 950°C. Clearly the initial reaction rates varied directly with mineral content of the coal. The demineralized sample was virtually unreactive with carbon dioxide. An acid washed (pH=0.8) sample reacted at 0.8 (g/gh) maf while a sample of raw lignite in which the exchangeable cations were replaced with ammonium ions reacted at 1.47 (g/gh) maf or 1.8 times as fast as the acid washed sample. The raw lignite char had the highest reactivity, as expected, at 8.46 (g/gh) maf. Apparently, the mineral cations associated with the organic part of the coal are able to catalyze the char-carbon dioxide reaction and therefore removing these cations reduces the char reactivity. It is difficult to suggest why the NH_4-form coal, in which it is assumed that all the exchangeable mineral cations were removed reacted faster than the acid washed coal. Possibly the discrete mineral phase plays a role in the catalysis of the reaction, also. Figure 20 shows that the CO_2 reactivity of Estevan lignite char from raw coal measured at 850°C was only 28 percent of that at 950°C.

Comparison of char reactivity in carbon dioxide between coals of different rank was also done. Figure 21 shows that the reactivity of Forestburg sub-bituminous #2 char was only 25 percent of that of Estevan lignite #4 under the same test conditions. Acid washing (pH=1.5) of the Forestburg coal reduced the char reactivity by 80 percent to 0.44 (g/gh) maf as shown in Figure 22. The reactivity of Balmer bituminous #2char in carbon

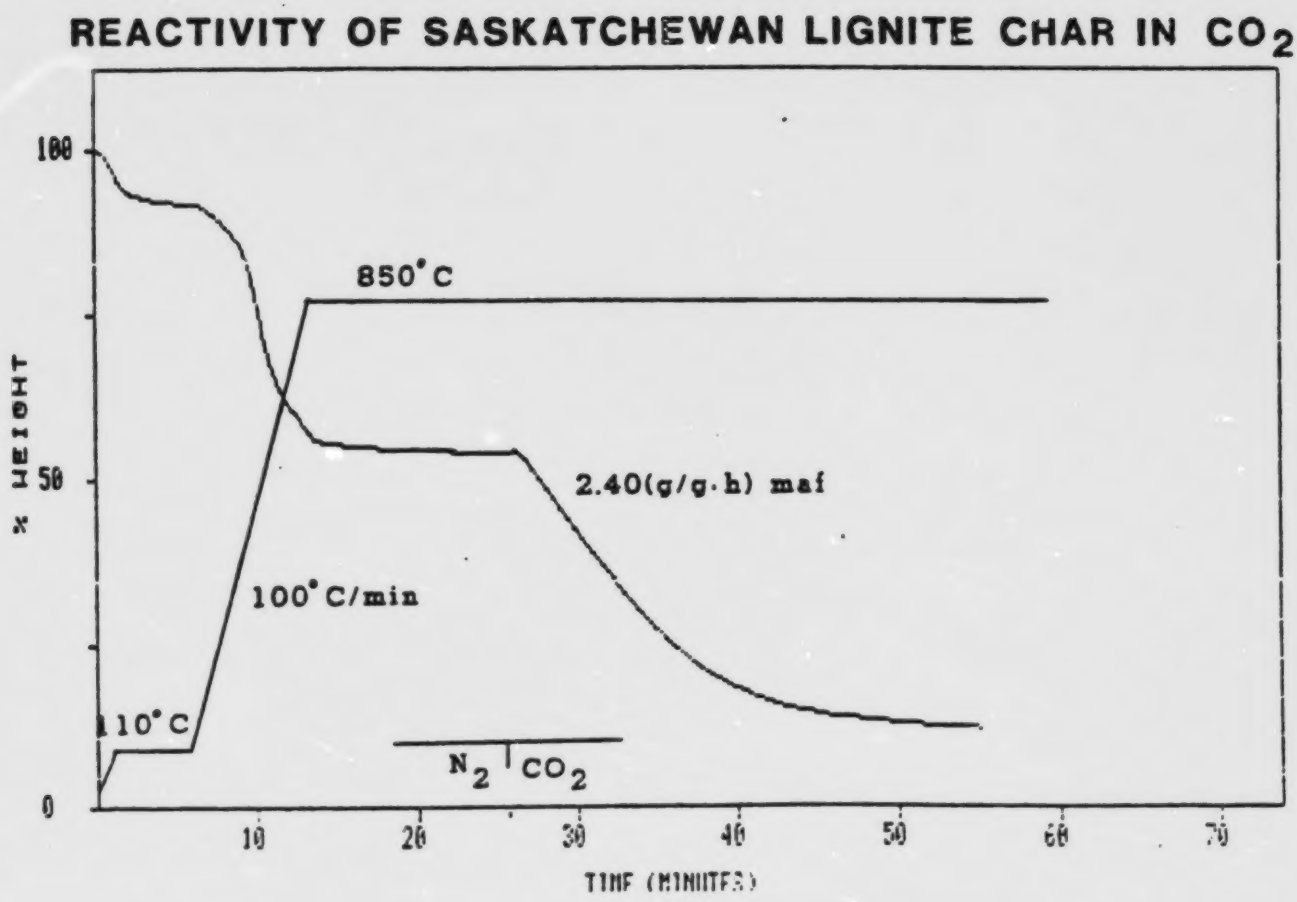

Figure 20 Reactivity of Estevan Lignite #4 Char in CO_2

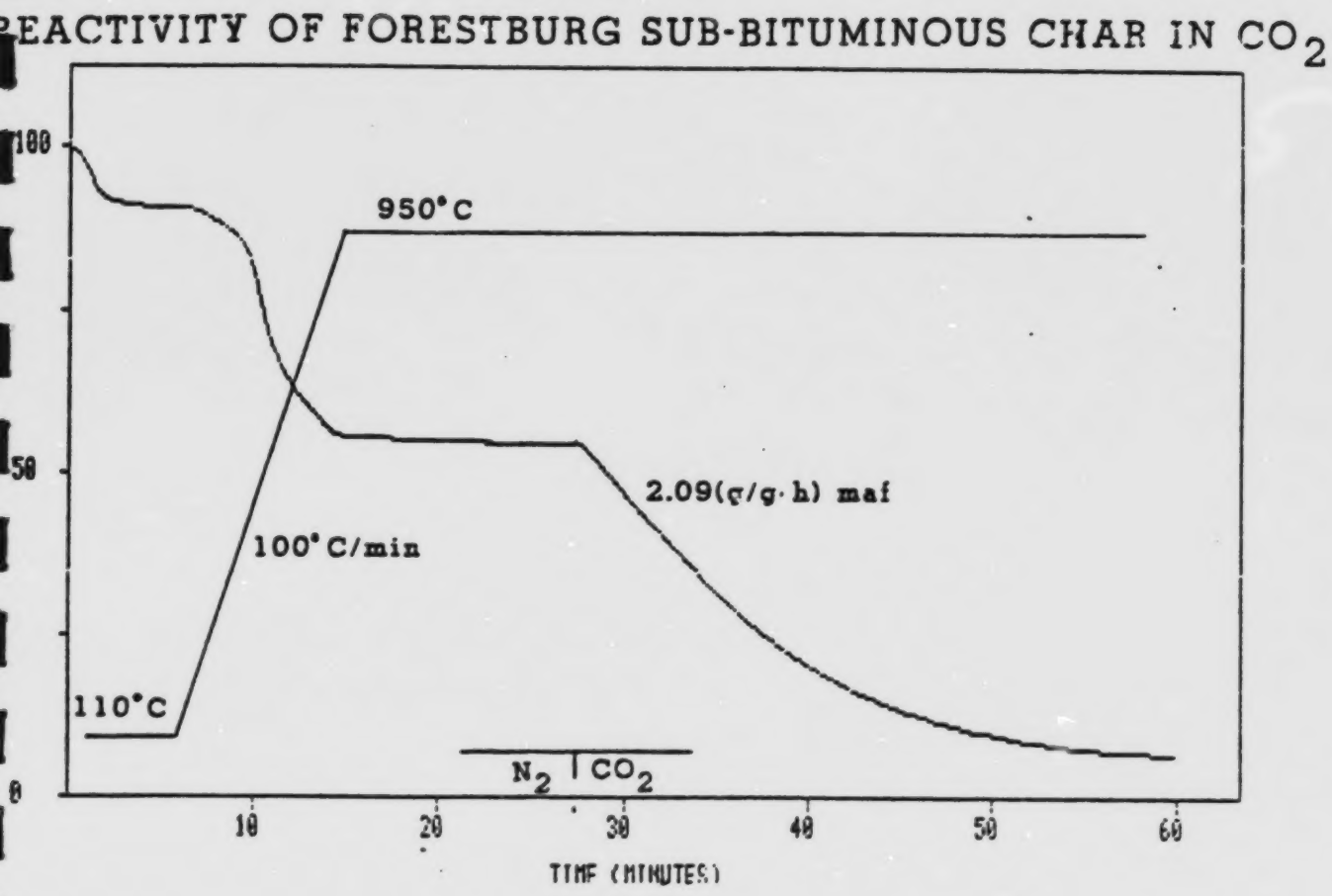

Figure 21 Reactivity of Forestburg Sub-Bituminous #2 Char in CO_2

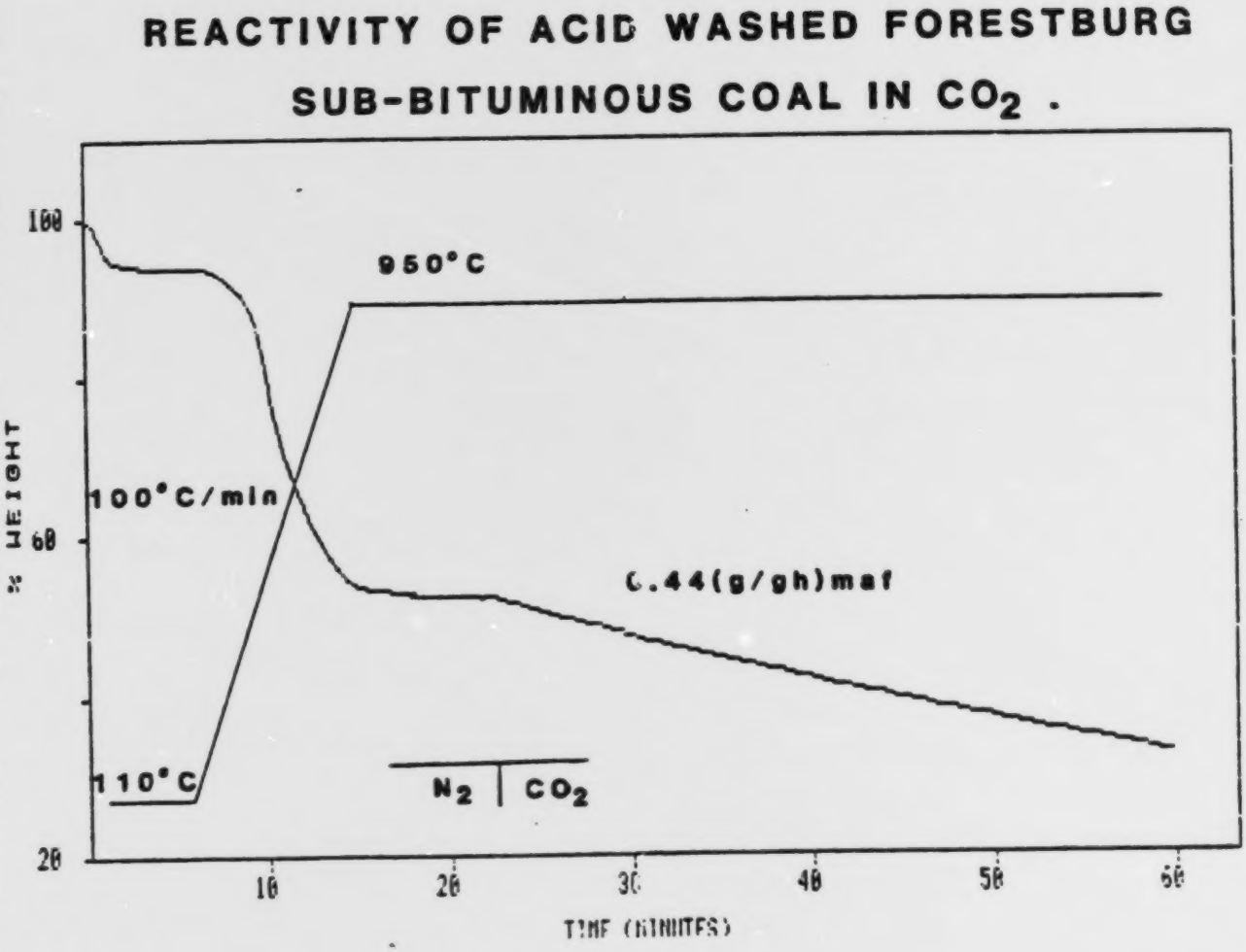

Figure 22 Reactivity of Acid Washed Forestburg Sub-Bituminous #2 Coal in CO_2

dioxide at 950°C is shown in Figure 23. It was virtually unreactive with an initial rate of only 0.04 (g/gh) maf. These results show clearly that the gasification reactivity of chars from raw coal was strongly dependent on coal rank. However, altering the mineral content of a coal by acid washing changes this dependence on rank. The initial char reactivities of demineralized lignite, of acid washed sub-bituminous, and of raw bituminous coals were low and very similar [0-0.44 (g/gh) maf]. Thus, it appears that the dependence of char reactivity on parent coal rank can be attributed primarily to the relative effectiveness of the inherent catalytic activity of the inorganic material in the coal. These inorganic cations have a maximum catalytic effect when they are associated with the organic structures of the coal e.g. in lignite, and show negligible catalytic effect when present as discrete mineral matter e.g. as in Balmer bituminous coal.

Table 14 also shows the proximate analysis of two chars produced by pyrolysis of an acid washed Forestburg sample (Run 168). During the run nearly 20 grams of char were blown past the char pot and into the cold condensers. The other 23 grams of char were collected in the hot char pot. The results in Table 14 show that the char which was kept at reaction temperature in the char pot during the run underwent a greater degree of devolatilization than did the char which collected in the condensers. The volatiles which would normally have been produced from the char in the condensers account for the lower volatile product yields (i.e. higher char yield) of Run 168

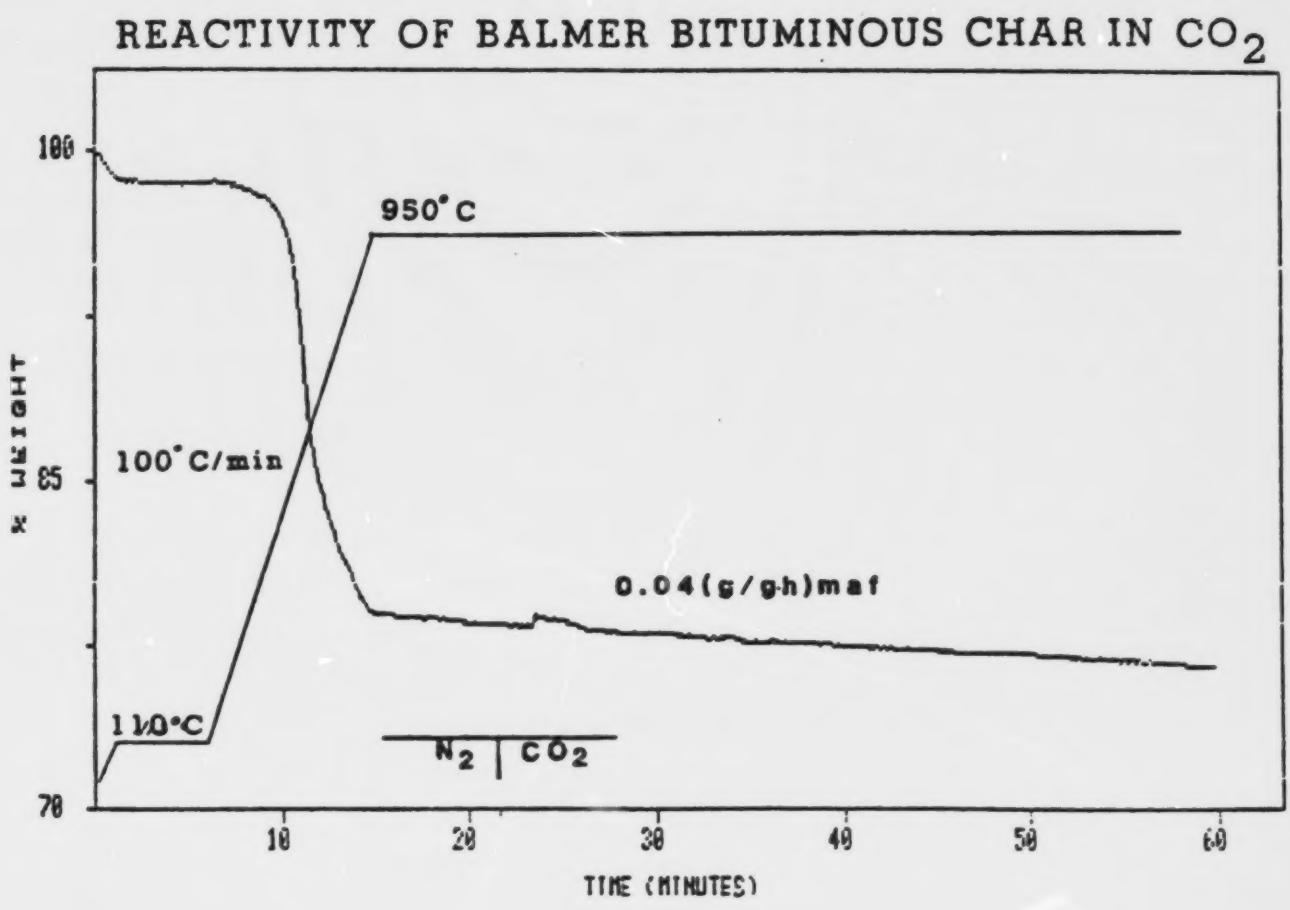

Figure 23 Reactivity of Balmer Bituminous #2 Char in CO_2

compared to Run 158.

Petrographic analyses of the Estevan lignite and Forestburg sub-bituminous coals were also carried out by the Department of Geology, University of Regina, Saskatchewan. Five chars, three from acid washed Estevan, lignite #4, and one each from raw lignite #4 and raw Forestburg #2 coal, were also analyzed. The detailed report of these analyses is given in the Appendix. A summary of the results is shown in Tables 40 and 41 and in Figure 24. In petrographic terms, the Estevan lignite and the Forestburg sub-bituminous coal showed only minor differences, as did the petrography of the chars. Temperature of pyrolysis appeared to be the most important parameter.

Maceral Group %	Estevan coal	Forestburg coal
Vitrinites Huminites	86.2	88.8
Liptinites	6.2	4.0
Inertinites	4.8	5.4
Mineral Matter	2.8	1.8
	100.0%	100.0%
% Reflectance; R_o random	0.36%	0.46%

Table 40 Petrographic analysis of coal pyrolysis feedstocks (WRI)

Sample No: % residue component	171	163	166	167	158
Unaltered coal	0.0	0.2	0.0	0.2	0.6
Altered coal					
(i) isotropic					
- non vesicular	3.2	1.0	4.8	11.6	2.0
- vesicular	88.0	84.6	84.8	85.8	78.4
- highly vesicular	7.8	13.2	9.6	0.4	18.8
(ii) anisotropic	1.0	0.8	0.6	0.8	0.0
Mineral matter	0.0	0.2	0.2	1.2	0.2
	100.0 %	100.0%	100.0%	100.0 %	100.0%
% Reflectance, R_o random	3.9	3.6	3.7	2.5	3.4

Table 41 Petrographic analyses of coal pyrolysis residues generated by the Waterloo Research Institute

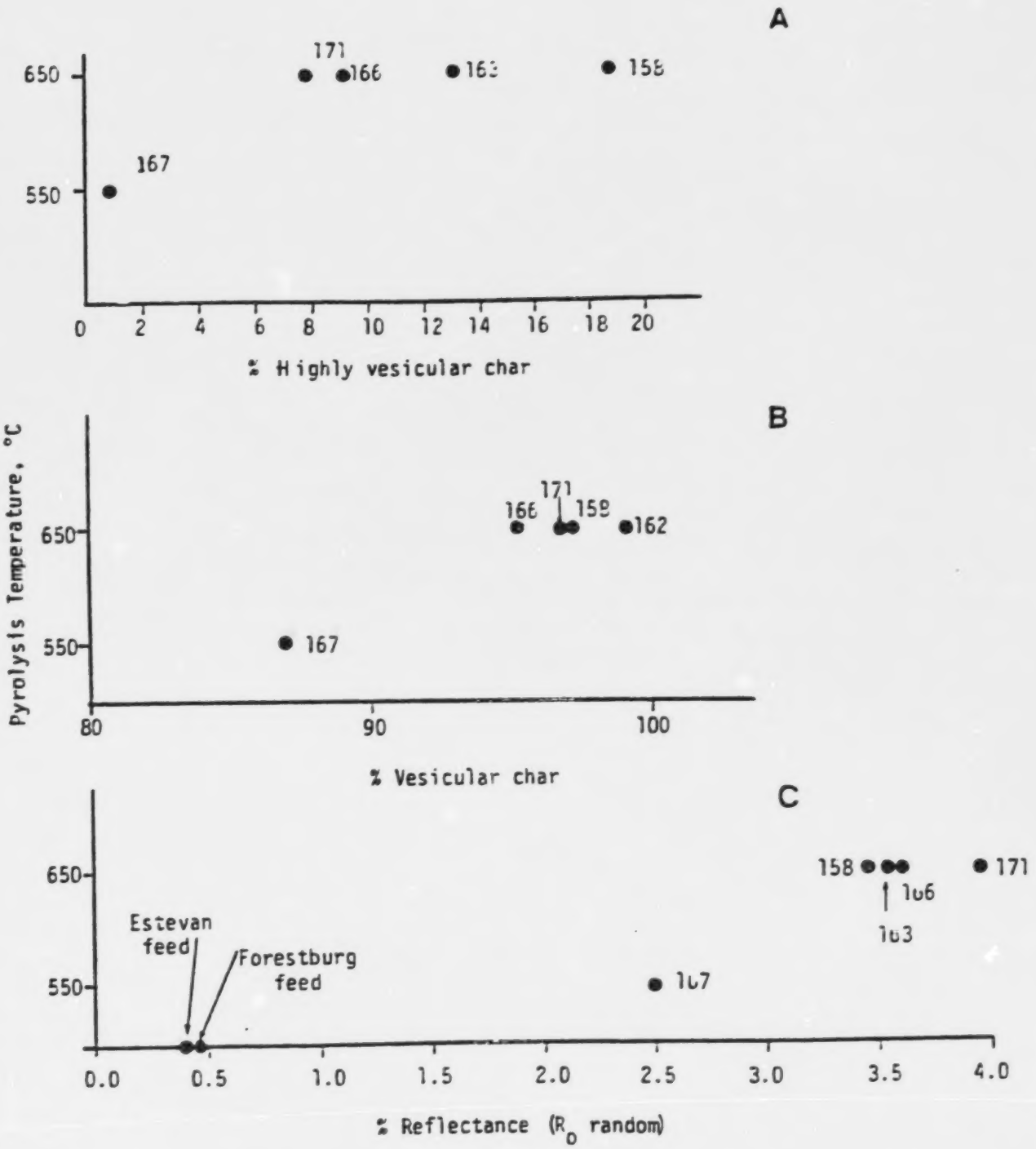

Figure 24 Pyrolysis temperature versus % highly vesicular char (A), % vesicular char (B) and reflectance (C).

CONCLUSIONS

1. Tar liquid yields were substantially improved from Saskatchewan (Estevan) lignites or from Alberta (Forestburg) sub-bituminous coal by removing the alkaline earth cations associated with the organic coal matrix. These cations were removed by an ion exchange process by acid washing to a pH of 1.5 to 2.5. The improvement in tar yields, of up to 50%, depends directly on the amount of exchangeable cations per kg. of dry coal. In general, improvement in tar yield was in the order lignites > sub-bituminous C > sub-bituminous B > bituminous. The latter coal (Balmer) showed very little benefit from acid washing. Acid consumption was about 1.1 to 1.2 times the equivalent amount of cations removed. Any appropriate acid can be used e.g. HCl, H_2SO_4, H_2SO_3. The removal of exchangeable cations increased tar yield at the expense of gas yield, particularly CO_2. The gasification effectiveness of these organically bound cations was calcium > magnesium > potassium > sodium. Iron and aluminum were not exchangeable and were not removed by acid washing.

2. Acid washing of lignite or sub-bituminous coal resulted in a significant de-ashing - 60% removal for Estevan lignite and 44% for Forestburg sub-bituminous coal. Hat Creek sub-bituminous coal had a very high ash (clay) content, and benefits of acid washing were minimal. Tar product quality was about the same from raw or acid treated coal.

3. An order of magnitude estimate of the costs of acid washing a lignite coal indicate that the cost of recovery of the

incremental tar produced depends to a large extent on acid cost. With an order of magnitude allowance for processing cost of the acid washing step, for sulfuric acid at $100/t, the incremental tar costs $33/bbl. (42 U.S.gallons), for acid at $50/t, the tar costs $20/bbl., for acid at $25/t, the tar costs $14/bbl. and for waste acid the cost of the incremental tar production would be $7/bbl. No credit is taken for de-ashing. The spent acid wash solution would be inocuous and would require only some aeration to remove trace organic matter.

4. Flash pyrolysis of coal in a steam atmosphere does not appear to offer any advantage in achieving a higher tar yield; and may in fact reduce tar yields slightly because a steam-tar reforming reaction appears to occur to a small degree at optimal flash pyrolysis conditions. This conclusion agrees with work at CSIRO (Australia).

5. Lower rank coals were pyrolyzed without difficulty in a larger scale unit (1.5 kg/hr), and in particular, lignite was treated with no operating problems in our normal unit.
Higher rank coals e.g. sub-bituminous C coal require some modifications to product collecting systems because of the stable tar fogs formed. Other workers have found oil scrubbers or electrostatic precipitators to be more suitable than the surface condensers used in the present work. Initial tests with an electrostatic precipitator during pyrolysis of a Forestburg sub-bituminous coal gave good results.

6. Yields of tar in the larger scale unit were higher for

lignite than in the bench scale unit, but lower for sub-bituminous coal. The latter result may be in error due to product collection problems. Recycling of product gases without removal of C_2 + or BTX fractions, as was done in these tests, also reduces the yields of liquid products. It is expected that the bench scale and larger continuous unit will give the same yields at comparable operating conditions. Electrostatic precipitators or liquid scrubbers are probably necessary for liquid product collection in continuous operation.

7. Attempts to control the agglomeration of caking coals in a fluid bed reactor by pre-oxidation were successful only if pre-oxidation was extensive, and some reduction in tar yield then resulted. The free swelling index appears to be a reasonable indicator of agglomeration behaviour. Tentatively, this index should not be more than 1 to 1.5 to avoid operating problems.

Blends of caking and non-caking coals were also pyrolyzed in an attempt to control agglomeration. Again, this approach can be used if the FSI of the blend is low enough, which usually means that the blend has to contain a higher proportion of non-caking coal than of caking coal.

Work by others suggests that spouted bed operation may be able to pyrolyze coals with FSI values to 3.0 or 3.5.

8. The relative reactivity of coals or of coal chars can be readily assessed by thermal gravimetric analysis using CO_2 as the reactant gas. The effect of the presence or absence of various types of mineral content can be readily shown. Mineral cations associated with the organic coal matrix in ion exchangeable form

catalyze the reaction of coal char. Chars from lignite coal, particularly, are very reactive due to the inherent catalytic action of this type of mineral matter. When it is removed by acid washing, a much less reactive char results. Higher rank coals, in which alkali or alkaline earth cations do not exist in ion exchangeable form, give relatively unreactive chars.

9. Tests with a caking bituminous coal (Sukunka) indicate that little benefit is achieved through pyrolysis in a CO_2 atmosphere. Tar yield was not significantly increased, and agglomeration problems were not improved.

10. Pyrolysis of acid washed lignites or acid-washed sub-bituminous coals in CO_2 did not significantly affect tar yields or product quality.

11. Measurement of the carboxylic acid content of lignite suggests that only about one half of these groups are ion exchange centres for mineral cations.

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APPENDIX A

Sample Calculation - Acid Usage

Acid Usage - Sample Calculation

Acid Washing of Forestburg Sample #2

Original Coal	350.05 g
Water Content	38.72 g
Dry Coal	311.33 g

320 ml of distilled water in slurry
added 42.2 ml 6.0 N HCl to bring pH to 1.5 from 6.19

Acid Required to Drop pH of Slurry

Original $[H^+] = 10^{-6.19}$ M => 320 ml $\therefore$ $\frac{320\text{ml}}{1000\text{ml}} \left| \frac{1}{} \right| 10^{-6.19}\text{mol} = 2.066(10^{-7})\text{mol of } H^+$

Final $[H^+] = 10^{-1.5}$ M => 320 ml $\therefore$ $\frac{320\text{ml}}{1000\text{ml}} \left| \frac{1}{} \right| 10^{-1.5}\text{mol} = 1.0119(10^{-2})\text{mol of } H^+$

$\therefore$ $[1.0119\ (10^{-2}) - 2.066\ (10^{-7})]$ mol of H^+ added

$= 1.0119\ (10^{-2})$ mol of H^+

$$\frac{1.0119(10^{-2})\text{ mol } H^+}{} \left| \frac{1}{6.0\text{ mol HCl}} \right| \frac{1000\text{ ml}}{1} = 1.7\text{ ml of 6N HCl req'd to lower pH}$$

Acid Reacted per weight of fresh dry coal

$$\frac{(42.2-1.7)\text{ml}}{} \left| \frac{6.0\text{ mol HCl}}{1} \right| \frac{1\text{ eq } H^+}{\text{mol HCl}} \left| \frac{1}{1000\text{ ml}} \right| \frac{}{311.33\text{ g dry coal}} \left| \frac{1000\text{ g}}{\text{kg}} \right| = 0.781 \frac{\text{eq}}{\text{kg dry coal}}$$

APPENDIX B

Petrographic Analysis of Coals and Flash Pyrolysis Chars Generated by the Waterloo Research Institute

CHAPTER 4

CHARACTERISATION OF CHARS PRODUCED BY COAL FLASH PYROLYSIS

4.1. Introduction

The Waterloo Research Institute submitted two coals and five char samples for petrographic analysis. The coal pyrolysis feedstocks were samples of Estevan and Forestburg coal. Three of the chars were produced by pyrolysis of Estevan coal that had been acid washed to remove some of the mineral matter. The remainder were products of the pyrolysis of unwashed Estevan and Forestburg coals. Four of the chars were generated at 650°C and one at 550°C. The sample numbers and descriptions are recorded in Table 4.1.

The coal feedstocks were analysed according to the modified I.C.C.P. maceral classification shown in Table 2.2. The char components were divided into unaltered coal, isotropic and anisotropic altered coal and mineral matter, according to the residue classification in Table 2.3. The chars were also characterised according to their vesicular or non-vesicular appearance. Vesiculation (the presence of pores or holes) was produced when gaseous products were generated from the coal. It is common for coal pyrolysis chars to exhibit vesiculation. The extent and type of vesiculation depends upon the pyrolysis temperature (Energy Research Unit, 1984).

Reflectance data were obtained on huminite macerals in the coal feedstocks and huminite products of the chars; mean values were recorded and ranges are represented by reflectograms.

Char No.	171	163	166	167	158
Coal feed:	Estevan lignite				Forestburg sub-bituminous
Coal Condition:	raw	acid washed			raw
pH of slurry	-	0.8	4.0	4.0	-
Pyrolysis temp.°C	650	650	650	550	650

Table 4.1: Nature of the coal feed and pyrolysis conditions (WRI)

4.2. Petrographic characterisation of the residues

4.2.1. Altered coal

Altered coal comprised morphologically or optically altered coal coal macerals; often only the reflectance differed. Liptinite macerals were very reactive and were eliminated by pyrolysis. Inertinite macerals werevariably inert or semi-inert and contributed to the unaltered or altered coal. Altered inertinites were detected by changes in reflectance.

The inertinite contents of the chars comprised only the 'discernable' inertinite macerals represented by highly reflecting fusinite. Once the reflectance of the huminite/vitrinite exceeds or approximates that of the inertinite (2.0% R_o random) it becomes more difficult, and in some cases impossible, to differentiate between inertinite and vitrinite chars. As a result only the inertinites having an initial reflectance greater than the maximum reflectance attained by the huminite/vitrinite chars were visible (see reflectograms in Appendix B). In the feed coal, such inertinite is called pyrofusinite. The huminite macerals were variously reactive and underwent morphological, optical and reflectivity changes. They also became vesicular as a result of the loss of volatile compounds. The altered vitrinitic (huminite-derived) char components were classed as 'non-vesicular' (Plate 2a) when they showed no vesiculation or porosity other than that exhibited by the original coal macerals. (The densinite or groundmass huminite macerals can be quite porous). Vesicular chars were repeatedly ruptured by the evolution of volatile products (Plate 2b); structured huminites, being more reactive than other huminite macerals (Energy Research Unit, 1984), commonly produce this type of char.

'Highly vesicular' chars had large pores or holes which partly or completely destroyed the interior of the particle (Plates 2c, 2d, 2e). This type of vesiculation was produced by rapid and extensive devolatilisation of the coal. Structured huminite macerals produce highly vesicular chars.

The altered coal products were either isotropic or anisotropic. The isotropic products comprised highly reflecting chars (semicokes). The reflectance was greater than 2.5% R_O random, and commonly greater than 3.0%. The anisotropic residues (Plate 2e) resembled the cokes produced by coal carbonisation rather than the semicokes generated by low temperature coal conversion processes.

4.3. Results and Discussion

4.31. Coal Feedstocks

4.31.1. Estevan coal

The petrographic characteristics of the Estevan and Forestburg coal feedstocks are given in Table 4.2. The Estevan coal was a huminite-rich lignite. Huminites are reactive coal macerals and, because they are usually the most abundant macerals in low rank, humic coals, they are the principal source of coal liquids. The structured huminite macerals are the most reactive and these accounted for half of the coal (50.8%) and nearly 60% of the total huminites.

Liptinite macerals are the most reactive; these accounted for 6.2% of the coal which is about average for Estevan lignite.

Maceral Group %	Estevan coal	Forestburg coal
Vitrinites Huminites	86.2	88.8
Liptinites	6.2	4.0
Inertinites	4.8	5.4
Mineral Matter	2.8	1.8
	100.0%	100.0%
% Reflectance; R_o random	0.36%	0.46%

Table 4.2: Petrographic analysis of coal pyrolysis feedstocks (WRI)

Inertinite macerals constituted only 4.0% of the coal. Semi-inert macerals such as semifusinite, although they were probably reactive, comprised only 1.8% of the total coal and therefore will not have contributed significantly to yields.

Mineral matter constituted only 2.8% of the coal. Some of this was finely divided pyrite (FeS), which is difficult to remove from coal, and the remainder was mostly fine silica and clay minerals (1.0%). The reflectance of the huminite in Estevan coal was 0.36% R_o random, which indicates lignite.

4.31.2. Forestburg coal

The Forestburg coal had a similar composition to the Estevan but was higher in rank. The huminite/vitrinite content was high (88.8%) and 68% was reactive structured huminites/vitrinites. The liptinite content was lower than that of the Estevan coal (4.0%) so that less coal-derived liquid could be expected from the highly reactive liptinite macerals. Unreactive inertinite macerals constituted only 5.5% of the coal. Like the Estevan coal, only a small portion comprised semifusinite so that most of the inertinite macerals could be expected to concentrate in the solid residues.

The reflectance of the Forestburg coal was 0.46% R_o random indicating that it was sub-bituminous and significantly higher in rank than the Estevan coal.

4.32. Pyrolysis chars

The petrographic compositions, reflectograms and mean reflectance data are given in Appendix B. These are summarised in Table 4.3.

. Sample No: % residue component	171	163	166	167	158
Unaltered coal	0.0	0.2	0.0	0.2	0.6
Altered coal					
(i) isotropic					
- non vesicular	3.2	1.0	4.8	11.6	2.0
- vesicular	88.0	84.6	84.8	85.8	78.4
- highly vesicular	7.8	13.2	9.6	0.4	18.8
(ii) anisotropic	1.0	0.8	0.6	0.8	0.0
Mineral matter	0.0	0.2	0.2	1.2	0.2
	100.0 %	100.0%	100.0%	100.0 %	100.0%
% Reflectance, R_o random	3.9	3.6	3.7	2.5	3.4

Table 4.3: Petrographic analyses of coal pyrolysis residues generated by the Waterloo Research Institute

The products of both the Estevan and Forestburg coals were predominantly isotropic chars derived from huminite/vitrinite and inertinite macerals. No traces of liptinites were observed in any of the chars indicating that they were successfully converted.

Two of the chars (171 and 166) contained unaltered coal but in the other three <1% unaltered coal was recorded.

The chars comprised mostly isotropic altered coal which ranged from 95.4% to 98.0%. The remaining residue comprised inertinite (1.0% to 2.2%) and anisotropic, high temperature coke (0% to 1.0%). Two residues (166 and 167) contained small amounts of isotropic granular residues which vaguely resembled the type produced by low temperature coal liquefaction, except that the reflectivity was much higher.

Mineral matter was present in very small amounts (0.2%) in two chars from acid-washed coal (163 and 158); 167 comprised 1.2% mineral and none was recorded in 171, which was not acid washed. The mineral matter contents of the acid-washed chars represented 7% to 43% of the mineral contents of the feed coals (see Tables 4.2 and 4.3). As the Estevan coal feed contained only 2.8% mineral matter (determined by petrographic analysis) it is questionable whether or not the mineral contents of the chars are even significant. From the results obtained, it would seem that acid washing did not remove all of the mineral matter in the feed coal used for experiments 163 and 166; and just over half of the mineral in 167. On the other hand, the char from unwashed Estevan coal (171) did not contain any (detectable) mineral matter.

It is questionable whether petrographic analysis is sensitive enough to record the mineral contents of coals and coal products when

1) the mineral matter comprised clay minerals, silica and pyrite which were very finely divided throughout the coal, 2) the particle size of the mineral components was only a few micrometers or less than 1 , and 3) the accuracy of the point count method of analysis is theoretically ±1%, which makes assessment of low concentrations subjective.

The Forestburg coal char (158) contained only 0.2% mineral matter, which represented 11% of the concentration of mineral in the feed (1.8%). In this experiment, the coal was not acid-washed which suggests that some of the mineral matter was altered or destroyed by pyrolysis.

Optically anisotropic semicokes, which are common components of coal liquefaction residues, were absent from the flash pyrolysis chars. Very small quantities of anisotropic high-temperature coke (0.6% - 1.0%) similar to that produced by coal carbonisation, were present in four of the chars, especially those derived from Estevan coal. These were characteristically vesicular or highly vesicular.

4.33. Effects of experimental conditions

The effects of variable exprimental conditions on the petrographic characters of the solid products of coal flash pyrolysis were evaluated using two parameters: 1) the presence and extent of vesiculation in the char particles; and 2) the reflectance of the huminite/vitrinite chars.

4.33.1. Vesiculation

The relative proportions of non-vesicular, vesicular and highly vesicular vitrinite/huminite chars are shown in Table 4.3 and plotted against pyrolysis temperature in Figure 4.1. It is significant that the

char produced from Estevan coal at 550°C (167) did not contain highly vesicular huminite/vitrinite char whereas those produced at 650°C comprised between 7.8% and 18.8%. The most highly vesicular was the Forestburg product (158), produced at 650°C. This suggests that (i) the volume of gaseous products obtained during flash pyrolysis increased with increasing pyrolysis temperature; (ii) a greater volume of gas was obtained from Estevan coal at 650°C than at 550°C, and (iii) more gas was obtained from Forestburg coal at 650°C than from Estevan coal. .

It is interesting to note that the total amount of vesicular and highly vesicular char in each of the residues is approximately equal to the reactive maceral content (huminites/vitrinites plus liptinites) of the corresponding feed coals.

4.33.2. Reflectance

The mean reflectance values (R_o random) obtained on the pyrolysis chars from Estevan coal was 2.1% to 3.5% greater than that of the feed (0.39%). Likewise, the reflectance of the char (158) from Forestburg coal was 2.9% greater than the feed (0.46%). As the difference between the reflectance of a coal and its residue is an indication of the difference in carbon content, it follows that the pyrolysis chars were highly carbonaceous residues. These chars from Estevan and Forestburg coal at 650°C had higher reflectivities and were therefore considerably more carbonaceous than 167, produced at 550°C from Estevan coal. This suggests that the yields from 158, 166, 163 and 171 were greater than from 167. The most carbonaceous char was 171.

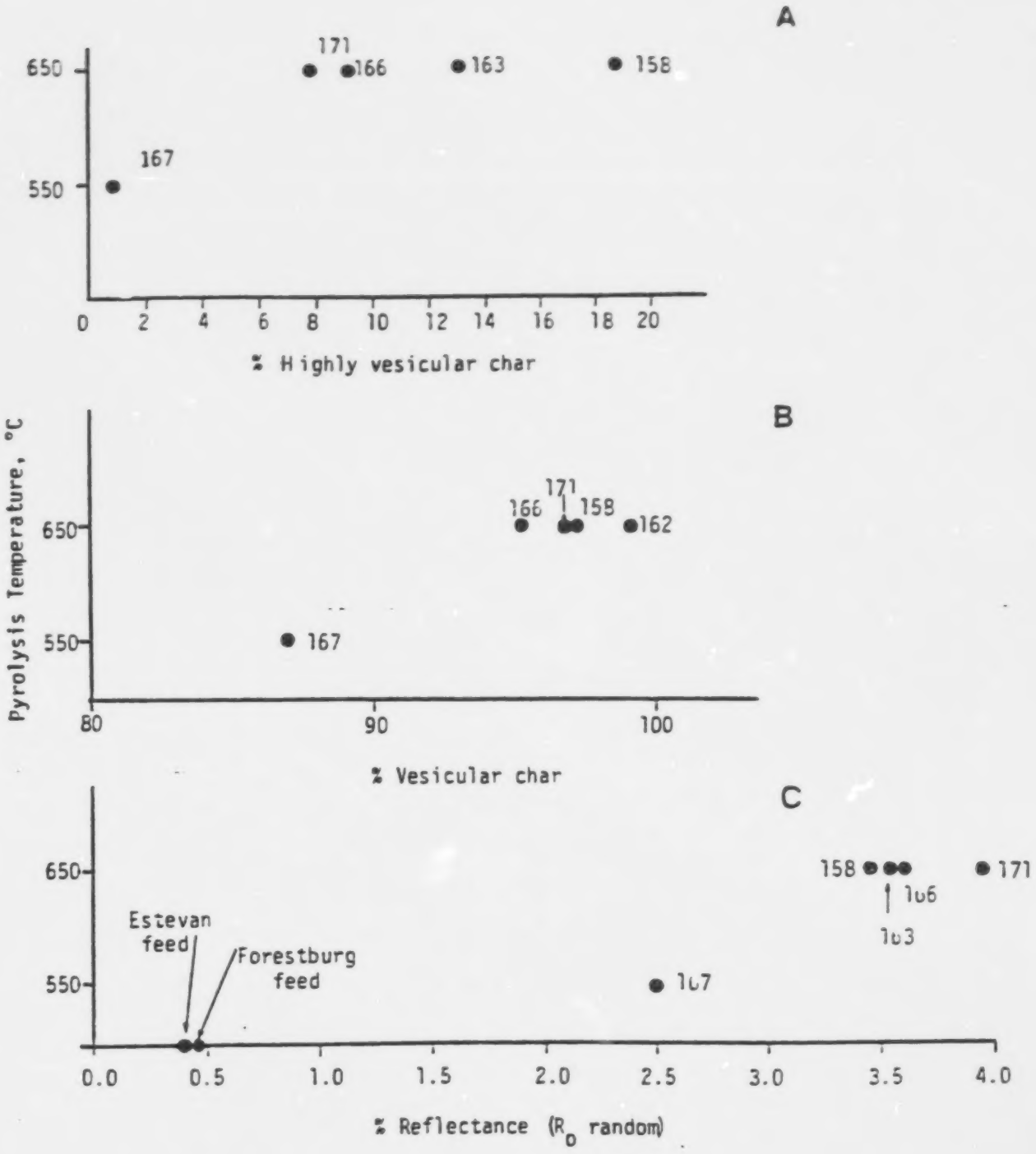

Figure 4.1: Pyrolysis temperature versus % highly vesicular char (A), % vesicular char (B) and reflectance (C).

The spread in reflectance values obtained from each sample is indicated by reflectograms (see Appendix B7-9). A broad range of reflectance was exhibited by the chars (2.0 to 4.99%). In previous reports of pyrolysis chars, altered coal with a reflectance of greater than 4% comprised 'highly altered coal' (Energy Research Unit, 1984). The distinction between 'altered' and highly altered' was more discernable. In this study the broad range of reflectance values exhibited by the chars makes it difficult to distinguish 'highly altered' and 'altered' components. From the reflectograms, it appears that highly altered char was absent from 167, occurred in minor amounts in 163, 166 and 171 and comprised a significant portion of 158.

4.4. Conclusions

The solid products of fluidised-bed flash pyrolysis of Forestburg and Estevan coals were highly carbonaceous, isotropic chars. Little or no unaltered coal was observed and optically anisotropic semicokes were absent, but minor amounts of high temperature coke were observed.

The residues were derived primarily from vitrinite/huminite macerals. The absence of liptinite macerals indicates that they were successfully converted. The extent of reactivity of inertinite macerals was not determined; detectable inertinites comprised only a small portion of the residues (<2%) and was approximately equal to the fusinite content of the feed coals. The vitrinite/huminite chars were variously vesicular and therefore huminites/vitrinites were the principal sources of gaseous products. Vesiculation was best developed in the chars produced at 650°C. Highly vesicular char, suggesting rapid

and extensive devolatilisation of the coal, was best developed in the Forestburg char (158) produced at 650°C. The Estevan coal chars produced at 650°C also contained significantly large quantities of highly vesicular char. The type and extent of vesiculation developed was dependant upon pyrolysis temperature and the petrographic character (rank and composition) of the feed coal.

The high reflectivity of the chars indicated that they were highly carbonaceous; the reflectance in all cases was considerably greater than the feed coal and also greater than residues produced by low temperature liquefaction and other pyrolysis methods. A large range of reflectance was observed for the isotropic chars in each case and from the reflectograms it is obvious that a portion of each char should be considered as 'highly altered' coal. The amount was difficult to discern by visual inspection. More carbonaceous residues were generated at 650°C than at 550°C indicating greater alteration of the coal at 650°C.

The effects of acid washing of the coal were not discernable by petrographic methods. The mineral matter contents of the chars were lower than those of their respective feed coals but the coal feeds themselves were relatively poor in mineral matter.

Petrographic analysis of coal feedstocks

Maceral, %	Estevan	Forestburg
Huminites:		
Structured	50.8	60.4
Unstructured	2.6	7.4
Groundmass	32.8	21.0
Liptinites:		
Sporinite	3.0	1.4
Resinite	0.8	1.2
Cutinite	0.2	0.4
Alginite	-	-
Suberinite	1.2	0.4
Liptodetrinite	1.0	0.6
Inertinites:		
Fusinite	1.0	1.0
Semifusinite	1.8	1.6
Macrinite	-	-
Semimacrinite	0.2	-
Sclerotinite	0.2	0.2
Inertodetrinite	1.4	2.6
Micrinite	0.2	-
Mineral Matter.		
Pyrite	-	0.2
Other	1.0	1.6
Contamination (higher R_o coal)	1.8	-
	100%	100%
% Reflectance.		
Mean % R_o (random):	0.36	0.46
Standard deviation.	0.06	0.08

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Appendix B2

Petrographic analysis of fluidized bed coal pyrolysis
Residue # 158

Components	%
I. Unaltered coal:	
Vitrinite	0.6
Inertinite	-
II. Altered coal - Isotropic:	
(i) Non-vesicular:	
- Vitrinite	0.8
- Inertinite	1.2
(ii) Vesicular:	
- Vitrinite	78.4
- Inertinite	-
(iii) Highly Vesicular:	
- Vitrinite	18.8
- Inertinite	-
III. Altered coal - Anisotropic:	
(i) Non-vesicular:	
- Vitrinite	-
- Inertinite	-
(ii) Vesicular:	
- Vitrinite	-
- Inertinite	-
(iii) Highly vesicular:	
- Vitrinite	-
- Inertinite	-
IV. Mineral Matter	0.2
	100%

Summary:		
	% Unaltered coal	0.6
	% Altered coal - non-vesicular	2.0
	% Altered coal - vesicular	78.4
	% Altered coal - highly vesicular	18.8
	% Anisotropic coal - non vesicular	-
	% Anisotropic coal - vesicular	-
	% Anisotropic coal - highly vesicular	-
	% Mineral Matter	0.2
		100%

% Reflectance:		
	Mean R_o random	3.35
	Range R_o random	2.02-4.50

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Appendix B3

Petrographic analysis of fluidized bed coal pyrolysis
Residue # 163

Components		%
I.	Unaltered coal:	
	Vitrinite	0.2
	Inertinite	-
II.	Altered coal - Isotropic:	
	(i) Non-vesicular:	
	- Vitrinite	-
	- Inertinite	1.0
	(ii) Vesicular:	
	- Vitrinite	84.6
	- Inertinite	-
	(iii) Highly Vesicular:	
	- Vitrinite	13.2
	- Inertinite	-
III.	Altered coal - Anisotropic:	
	(i) Non-vesicular:	
	- Vitrinite	-
	- Inertinite	-
	(ii) Vesicular:	
	- Vitrinite	0.4
	- Inertinite	-
	(iii) Highly vesicular:	
	- Vitrinite	0.4
	- Inertinite	-
IV.	Mineral Matter	0.2
		100%

Summary:		
	% Unaltered coal	0.2
	% Altered coal - non-vesicular	1.0
	% Altered coal - vesicular	84.6
	% Altered coal - highly vesicular	13.2
	% Anisotropic coal - non vesicular	-
	% Anisotropic coal - vesicular	0.4
	% Anisotropic coal - highly vesicular	0.4
	% Mineral Matter	0.2
		100%

% Reflectance:		
	Mean R_o random	3.60
	Range R_o random	2.54-4.40

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Appendix B4

Petrographic analysis of fluidized bed coal pyrolysis
Residue # 166

Components	%
I. Unaltered coal:	
Vitrinite	-
Inertinite	-
II. Altered coal - Isotropic:	
(i) Non-vesicular:	
- Vitrinite (1.2% granular)	3.0
- Inertinite	1.8
(ii) Vesicular:	
- Vitrinite	84.8
- Inertinite	-
(iii) Highly Vesicular:	
- Vitrinite	9.6
- Inertinite	-
III. Altered coal - Anisotropic:	
(i) Non-vesicular:	
- Vitrinite	-
- Inertinite	-
(ii) Vesicular:	
- Vitrinite	0.6
- Inertinite	-
(iii) Highly vesicular:	
- Vitrinite	-
- Inertinite	-
IV. Mineral Matter	0.2
	100%

Summary:	
% Unaltered coal	-
% Altered coal - non-vesicular	4.8
% Altered coal - vesicular	84.8
% Altered coal - highly vesicular	9.6
% Anisotropic coal - non vesicular	-
% Anisotropic coal - vesicular	0.6
% Anisotropic coal - highly vesicular	-
% Mineral Matter	0.2
	100%

% Reflectance:	
Mean R_o random	3.65
Range R_o random	2.55-4.10

Petrographic analysis of fluidized bed coal pyrolysis
Residue # 167

Components	%
I. Unaltered coal:	
Vitrinite	0.2
Inertinite	-
II. Altered coal - Isotropic:	
(i) Non-vesicular:	
- Vitrinite (1.6% granular)	9.4
- Inertinite	2.2
(ii) Vesicular:	
- Vitrinite	85.8
- Inertinite	-
(iii) Highly Vesicular.	
- Vitrinite	0.4
- Inertinite	-
III. Altered coal - Anisotropic:	
(i) Non-vesicular:	
- Vitrinite	-
- Inertinite	-
(ii) Vesicular:	
- Vitrinite	0.6
- Inertinite	-
(iii) Highly vesicular:	
- Vitrinite	0.2
- Inertinite	-
IV. Mineral Matter	1.2
	100%

Summary:	%
% Unaltered coal	0.2
% Altered coal - non-vesicular	11.6
% Altered coal - vesicular	85.8
% Altered coal - highly vesicular	0.4
% Anisotropic coal - non vesicular	-
% Anisotropic coal - vesicular	0.6
% Anisotropic coal - highly vesicular	0.2
% Mineral Matter	1.2
	100%

% Reflectance. Mean R_0 random 2.50
Range R_0 random 2.21-3.61

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Appendix B6

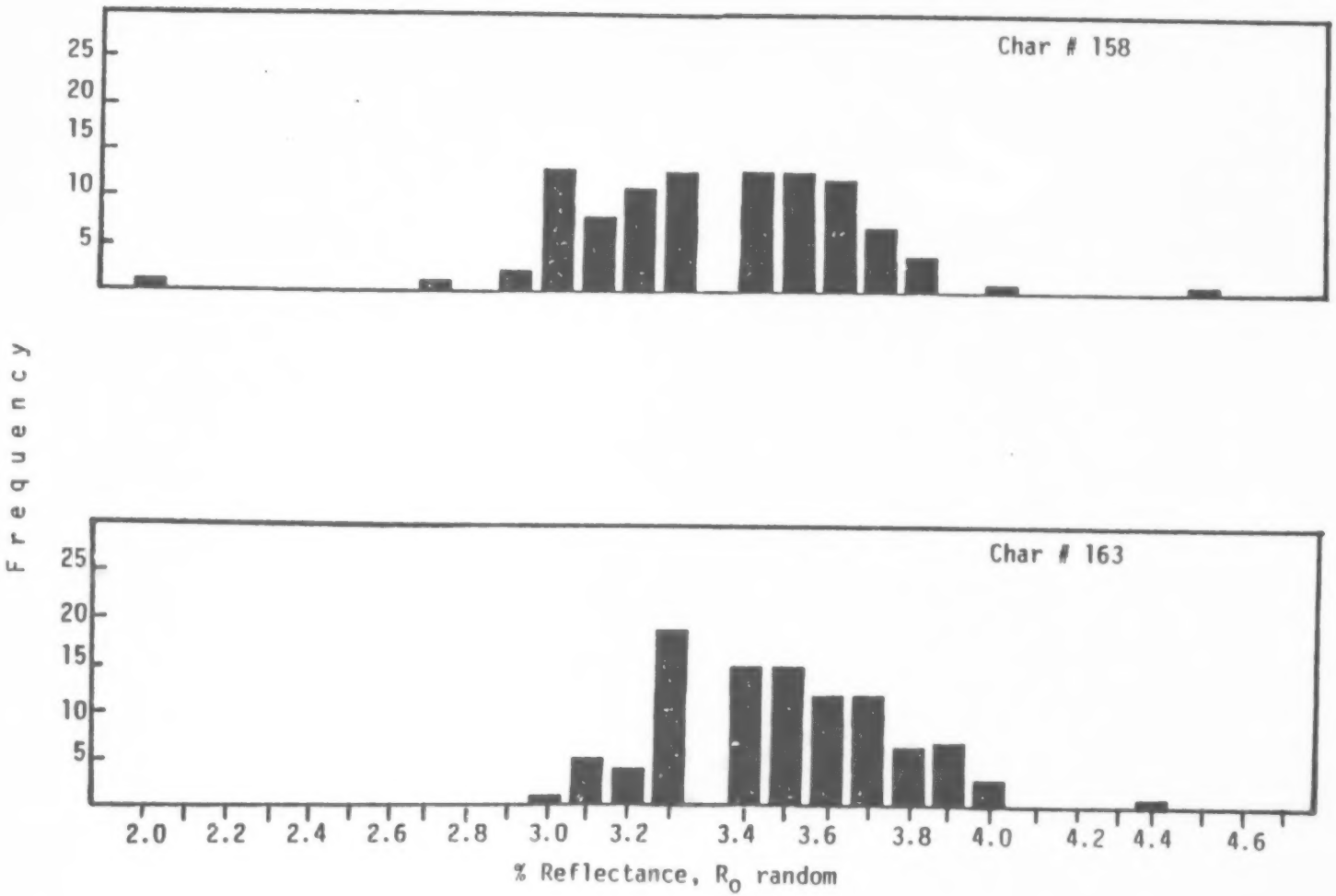
Petrographic analysis of fluidized bed coal pyrolysis
Residue # 171

Components	%
I. Unaltered coal:	
Vitrinite	-
Inertinite	-
II. Altered coal - Isotropic:	
(i) Non-vesicular:	
- Vitrinite	1.8
- Inertinite	1.4
(ii) Vesicular:	
- Vitrinite	88.0
- Inertinite	-
(iii) Highly Vesicular:	
- Vitrinite	7.8
- Inertinite	-
III. Altered coal - Anisotropic:	
(i) Non-vesicular:	
- Vitrinite	0.2
- Inertinite	-
(ii) Vesicular:	
- Vitrinite	0.8
- Inertinite	-
(iii) Highly vesicular:	
- Vitrinite	-
- Inertinite	-
IV. Mineral Matter	-
	100%

Summary:	
% Unaltered coal	-
% Altered coal - non-vesicular	3.2
% Altered coal - vesicular	88.0
% Altered coal - highly vesicular	7.8
% Anisotropic coal - non vesicular	0.2
% Anisotropic coal - vesicular	0.8
% Anisotropic coal - highly vesicular	-
% Mineral Matter	-
	100%

% Reflectance:	
Mean R_0 random	3.93
Range R_0 random	2.01-4.44

(ii) Reflectograms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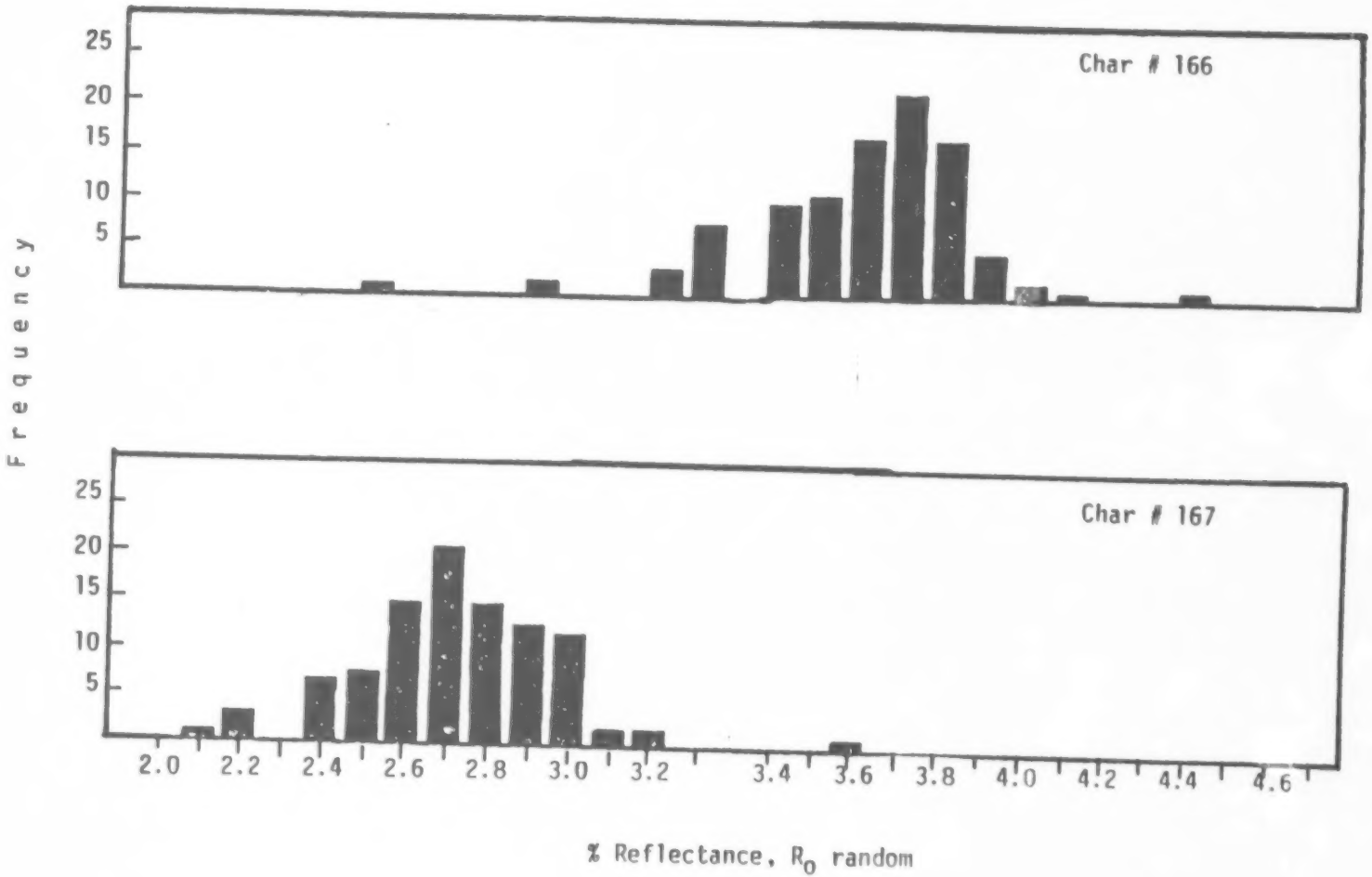
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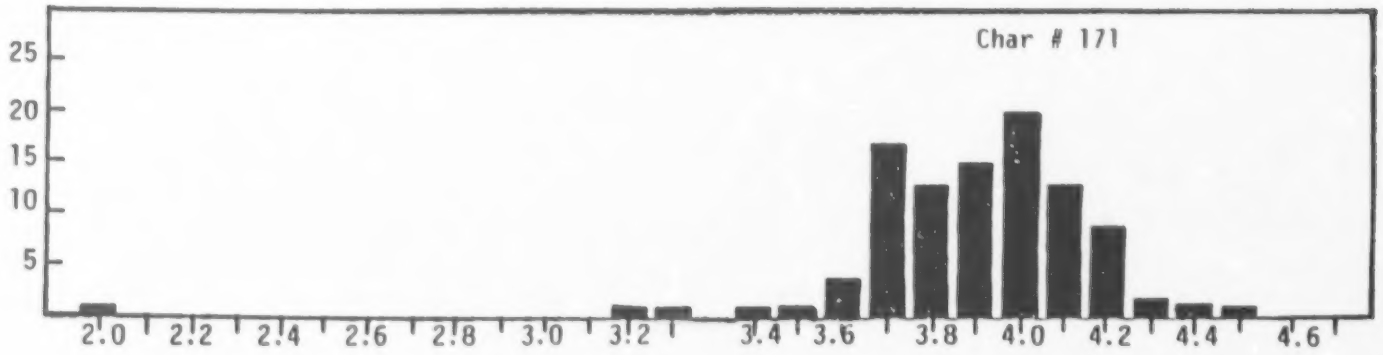
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APPENDIX C

Report of Visit to Australia - 1985

Summary of Visit to Australia

April, 1985

by D.S. Scott
Dept. of Chemical Engineering
University of Waterloo

General Comments Concerning Fossil Fuel Utilization in Australia

Australia is a nation which is not now deficient in energy, and which has adequate energy supplies for the future. In fact, Australia is at present an exporter of energy, and will continue to be so. However, like Canada, the sources of energy are not in balance with the energy use pattern, so that some difficulties arise which will require future changes, either in energy use pattern, or in the sources of energy. Australia faces a future shortage of liquid fuels, particularly for transportation, in the gasoline, diesel and jet fuel ranges. As well, Australia continues to be without adequate supplies of heavy oils, lubricating oils and asphalts, and this shortage will persist. At the present time, Australia is about 70% self-sufficient with respect to transportation fuels, but unless there are new major crude oil discoveries, oil supplies will decrease to 65% of requirements by 1990 and could fall to less than 20% by the year 2000. Therefore, although there is no current liquid fuel crisis, some action will be needed by the mid 1990's to prevent serious shortages in this energy category.

At the present time the total picture with regard to demand, fuel type used and reserves is shown in Table 1. The energy demand is projected to increase at from 2% to 2.4% per year to the year 2000. Note that Australia still retains its policy against the use of nuclear power, and uranium is produced for export only.

Table 1

Australian Energy Outlook for Fossil Fuels
1985 - 2000

Energy Demand, %	1985	2000
Industry & Other	34	31
Electricity generation	37	45
Transport	25	21
Domestic & Commercial	4	3

Energy Supply by Fuel Type, %*		
Coal	40	49
Hydro, Synfuels & Others	6	8
Gas	16	14
Oil	38	29

Energy Reserves, %*	
Coal	80.3
Gas	1.5
Oil	0.8
LPG	0.3
Uranium	17.1

Total Reserves 251.5×10^9 bbls oil equivalent
*Oil Shales, not included

Projected Energy Usage, % of reserves, 1984-2000	
Coal	6.5
Gas	46.0
Oil	176.0
LPG	133.0
Uranium	18.6

In summary, the present situation is that Australian crude oil supplies will be relatively constant until 1990, when rapid depletion will begin. Despite very active exploration in the last five years, oil discoveries have been small, although significant gas discoveries have been made. As a result, it is now ssumed that significant new supplies of liquid fuels will not be required before the year 2000, at which time a synthetic liquid fuel production rate of 35000-100000 bbls/day would be desirable. If some new minor oil discoveries are made, and synthetic liquid fuel production is established at the projected rate, Australia could remain 65%-75% self sufficient in liquid fuel production.

With respect to the production of synthetic liquid fuels, Australia has nearly all the possible alternative routes open. Large deposits of oil shale exist, and small scale research on pyrolysis processes for three of the main deposits is now underway. Coal is the largest resource, and large deposits of both brown coal and hign quality black coal are readily recoverable. Liquefaction and pyrolysis tests have been carried out for the last five years on coals from a number of the major deposits. Large quantities of natural gas in excess of projected domestic requirements exist in the north west, and could be used to produce methanol or to synthesize gasoline and other liquid fuels by other routes.

A good deal of applied research has been done in the 1980-85 period, on the utilization of alternate liquid fuels. Because of the great difficulty and high cost of converting the present gasoline distribution system, and the cost for engine

modifications, in the short to medium term it has been judged to be more economic to convert alternative fuels to gasoline rather than to use them as produced e.g. as CNG, methanol or ethanol. A good deal of work, both on the production and use of ethanol has been carried out in the last five years. Extensive motor tests with a 10% ethanol - 90% gasoline blend were judged to be successful. Production of ethanol from cellulose or cane sugar using bacteria with a high ethanol tolerance has also been developed. However, the cost of ethanol as a transportation fuel has been judged to be too high for the foreseeable future. As a result, government funding for research on ethanol production or use will be terminated shortly.

Because diesel oil and jet fuel fractions can both be produced by the Mobil methanol conversion process, and these two products are presently available only in very limited quantities from the very light Australian crudes, there is considerable interest in the New Zealand experiment with the Mobil process, and progress is being closely monitored. Again, this route is preferred to direct use of methanol because of the infrastructure conversion costs associated with wide-spread methanol usage. Some funding for fundamental C_1 chemistry research to produce diesel oils and other fuels is now being developed also (CSIRO - Fossil Fuel Div.).

A test program to use vegetable oils as diesel fuels has been pursued for three years and will be completed in 1985. Use of straight oils caused engine coking in only a few hours. Esterified oils could be used for up to 1000 hours of operation

before coking caused problems. With some engine redesign it is felt longer trouble-free runs will be possible (University of Melbourne, Dept. of Mechanical Engineering).

Exploration work on oil shale deposits has been done by Esso Australia under license from Southern and Central Pacific Corp. In addition, work has been funded at CSIRO (Division of Energy Chemistry, Lucas Heights) to develop a small fluid bed oil shale retorting process, and at the CSIRO Materials Science Division (Melbourne) to investigate upgrading of the shale oil.

The major source of funding for Australian research on alternative liquid fuels during the last five years has been the National Energy Research Development and Demonstration Council. As a result, this Council plays a very major role in deciding the course of research on alternate energy developments in both private and public institutions in Australia. Funding available has been somewhat reduced for the near future, and as a result a number of programs will be curtailed, particularly those dealing with direct coal liquefaction or coal pyrolysis, or eliminated, for example, ethanol production and fuel testing.

It is generally felt that new large scale synthetic fuel technology will not be required in Australia until 1995 to 2000, and demonstration scale plants for new technology may be established in that period. One brown coal liquefaction demonstration plant is now nearing start-up (NEDO plant in the La Trobe valley, Victoria, described in later sections) which is Japanese financed and operated. Apart from this project, it is unlikely that there will be any additional synthetic liquid fuel demonstration plants established in Australia in the next decade.

In summary, it is apparently now the consensus in Australia that a sufficient research effort has been made in evaluating the performance and yields obtainable from various Australian coals on a laboratory scale using acceptable liquefaction and flash pyrolysis technology. Upgrading research has yielded initial results for yields and qualities of transportation fuels obtainable. Work on liquefaction and upgrading technology will be continued but on a considerably reduced scale and oriented to very specific objectives e.g. diesel oil production.

New research efforts will be in the areas of novel technology e.g. direct oxidation of methane to methanol, or in coal combustion technology and oil shale retorting.

In Australia, much of the coal resources are owned by state electric utility companies. These organizations have little interest in developing synthetic liquid fuel technology from coal, although the Victoria State Energy Commission has now established the Coal Corporation of Victoria as a body to develop further commercial uses for brown coal. The R & D division of this new concern will be located at Morwell in the La Trobe valley (Dr. David Royston is Director of R & D). The Coal Corporation is also a partner in the Brown Coal Liquefaction (Victoria) Pty Ltd. (BCLV) being financed and operated by a Japanese consortium at Morwell, Victoria. The Queensland State Electricity Commission has also shown some interest in pyrolysis of bituminous coal, but has not pursued this extensively.

In summary, a lull of about five years duration, from 1985-90, can be expected to take place in Australian research into alternative liquid fuels. About 1990, if no major crude oil discoveries are made, research on coal and oil shale conversion will re-commence and will accelerate rapidly thereafter.

Report of Visit to

Brown Coal Liquefaction (Victoria) Pty. Ltd. (BCLV)
Morwell, Victoria, Australia

April 16th, 1985

by D.S. Scott
Dept. of Chemical Engineering
University of Waterloo

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Guides on Site:

Peter Brady
Ron (R.J.) Camier } Coal Corporation of Victoria

General - The chronology and administrative arrangements of the Brown Coal Liquefaction project using brown coal from the Loy Yang deposit, Morwell seam, located near Morwell, Victoria, are described in the attached brochure and reprint. In order to promote the uses of brown coal, and in particular, the non-electric power generation uses, a new council, the Coal Corporation of Victoria, was set up by the state of Victoria. This Council replaces the former Victoria Brown Coal Council. A description of the structure and terms of reference of the new Coal Corporation of Victoria is given in the attached Appendices, together with general technical details concerning the Loy Yang brown coal deposit. At the time

of the visit to Morwell the Coal Council was still in the preliminary stages of organization. However, they were acting as the Australian partner with the Japanese NEDO organization in the BCLV project. The principal role of the Coal Council appeared to be to supply the brown coal to the liquefaction plant. According to one source, the Coal Council was allowed by NEDO to have two observers attached to the actual liquefaction pilot plant operation, both of whom were analytical chemists (Camier and Brady). My observation was that they had only a superficial knowledge of the engineering aspects of the plant, although they clearly were scientifically well-informed. The entire pilot plant technical staff appeared to be Japanese, although the operators are Davy McKee Pacific Pty. Ltd.

My impression was that Australian academic, governmental and industrial technical people in the energy conversion area knew very little about BCLV. All process development was done in Japan, as was the pilot plant design. There was some resentment among the Australian scientific community at their virtual exclusion from this development (a great deal of work on brown coal liquefaction has been done in Australian laboratories). Also, some of the tactics of the Japanese relating to their energy development policies based on Australian resources drew highly unfavorable comment as well from scientific workers.

My general impression of the BCLV pilot plant was very good. At the time of the visit, commissioning tests for the first (SRC) stage were just being completed. Construction work had just begun (site development) for the second (liquefaction) phase, although this was apparently not a high priority.

The Research Division of the Coal Corporation of Victoria had just been established, and a Director of Research (Dr. David Royston) hired although he had not yet taken up his new duties. As a point of interest, Dr. Royston served a year with me as a post-doctoral fellow at the University of Waterloo.

Process Details

A process flow sheet is shown in the attached Figure with notes made on-site. The Stage 1 SRC unit will dry the brown coal in a steam heated rotary kiln, mainly because that was the only brown coal drying technology available at the time of plant design. A new NEDO development for de-watering slurries the wet coal with recycle oil, heats the slurry to evaporate water, and uses vapor recompression on the steam generated which then goes for slurry heating. Presumably this system will be installed at pilot plant scale in the future.* With the present kiln drying, nitrogen must be used because the hot dry brown coal ignites too readily in air.

The front end materials handling system for the raw brown coal appeared to be capable of moving much more than the nominal 50 t/day dry coal design capacity.

The primary hydrogenation reactor consisted of four columns in series, the first about 12 m high, the second and third 8.5 m high and the fourth 6 m high. Inside diameters varied from 60 - 80 cm. Coal particles were about 70 μm and it was stated that the reactors operated as slurry reactors in a transport mode. Heat control was by addition of cold gas - hydrogen or recycle gas. There was apparently no interstage removal or separation between

* The new drying system is shown in Figure 2 of the attached publication K. Kunii, T. Matsumura and R.J. Camier, Chem. Eng. Australia, ChE 9, No. 3, pp. 24-28, Sept., 1984. This system is not a part of the BCLV pilot plant, but is proposed.

reactor vessels. The guides (Australians from the Coal Corp.) were not too well versed in reactor matters, but felt that the series reactors were required because of the mechanism of the hydrogenation reactions. With respect to solids behavior in the reactor, apparently a bottom solids withdrawal is used, but these solids are then reinjected into the reactor as an aid in controlling the growth of particulates. There is no solids rejection at this point - all the ash appears in the primary SRC product. Calcium in the coal feed is the main cause of agglomeration of solids in the primary reactor, and there is a need to control ash composition so the agglomeration is manageable, although not preventable.

The catalyst is an iron oxide (probably red mud) plus sulfur. Different iron oxides are stated to change product yields. Sulfur is recovered for recycle from the H_2S in the off-gas. (A complete packaged Claus recovery unit was on site, not shown on the flow-sheet.) Oxygen rejection in the primary hydrogenation was stated to be about 50% as H_2O and 50% as CO_2 with some CO production also.

Stage 1 is expected to yield about 25 t/d of SRC and about 5 t/d of naphtha. Ultimately, the two stage liquefaction system is expected to yield about 71% of liquids.

A report on environmental consequences is available "Proposed Pilot Plant at Morwell - Environmental Effects Statement and Draft Environmental Impact Statement" prepared by Kinhill Pty. Ltd., 530 Little Collins Street, Melbourne 3000, Australia for Brown Coal Liquefaction (Victoria) Pty. Ltd. and dated July 27th, 1981.

A report on brown coal de-watering technology has been prepared by Davy-McKee Pacific Pty. Ltd. for the Victoria Brown Coal Council (now the Coal Corp. of Victoria) and was submitted in 1984. At the time of the visit, this report was not generally available.

In summary, the progress of this pilot plant will be worth following. Visitors to the site receive quite open treatment and discussion, and therefore periodic site visits are well worthwhile for those interested in liquefaction of low rank coals.

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Construction and commissioning of the BCLV pilot plant

T. Matsumura

K. Kunii

By K. Kunii, T. Matsumura and R.J. Camier

This paper describes the current status of construction and commissioning of the 50t/d (dry coal) liquefaction pilot plant which is funded by the New Energy Development Organisation (NEDO) of the Japanese Government, and is being undertaken in Australia by Brown Coal Liquefaction (Victoria) Pty Ltd (BCLV). The history of the project, and the nature of the technology which has been developed by Nippon Brown Coal Liquefaction Co Ltd (NBCL) are also outlined.

R.J. Camier

Introduction

The primary purpose of the BCLV pilot plant project at Morwell, Victoria is to develop and scale up a technology for the direct hydrogenation of brown coal to liquid fuels. Related objectives include:

- ☐ Establishment of operational techniques
- ☐ Confirmation of the quality of coal liquids
- ☐ Determination of environmental protection requirements
- ☐ Evaluation of the economic feasibility of the process.

The 50t/d size of the pilot plant represents a scale-up of about 100 times over the size of several process development units which have been in operation since 1979 at the Kobe Steel Mechanical Engineering Research Laboratories. Depending on the successful outcome of the pilot plant project, the next step would involve a further scale up of 100 times to a 5000t/d demonstration plant. This in turn would represent the first of about six trains in a commercial plant consuming 37,000t/d of dry coal, or 32Mt/a of raw coal (including raw coal for implant fuel). Despite the magnitude of this figure, it should be noted that during its operational life, such a plant would consume less than 3% of Victoria's readily available brown coal or less than 0.5% of its total resource.

The pilot plant will employ approximately 180 persons, of whom about 70% will be Australian. The peak contract construction workforce will be about 450. Shutdown maintenance will also be on a contract basis with a maximum employment of about 200.

It is projected that the pilot plant project, which is estimated to cost in excess of $A250 million, will operate through to 1988. In view of the long lead time for construction of such a major project, it is anticipated that commercialisation could take place early in the 21st century, coinciding with a projected downturn in world crude oil supplies.

Historical background

In the early 1970s, the Japanese iron and steel industry was facing a world shortage of high grade coking coals suitable for metallurgical coke production. This situation stimulated a Japanese consortium comprising Kobe Steel Ltd, Mitsubishi Chemical Industries Ltd and Nissho Iwai Corp to investigate the hydrogenation of Victorian brown coal to produce Solvent Refined Coal (SRC). The consortium, "KOMINIC", commenced experiments using a small autoclave reactor in 1971, and tests showed that the product SRC was suitable for blending with low grade coking coals to manufacture metallurgical coke. Although this research was completed successfully with SASOL's collaboration by 1978, the OPEC oil crises of 1973 and 1979 prompted the redirection of the project towards production of liquid fuels for transportation and industry.

In 1980 an expanded consortium, NBCL was formed by the addition of two oil companies, Idemitsu Kosan Co Ltd and Asia Oil Co Ltd. Concurrently the Japanese Government established NEDO to promote the development of new non-nuclear energy sources such as solar, geothermal, wind, hydrogen and coal conversion. This program, known as the "Sunshine Project" officially took up sponsorship of the NBCL process in 1981. NBCL was entrusted with the actual implementation of the project, and an Australian subsidiary, BCLV, was formed in order to carry out the construction and operation of a 150t/d (raw coal basis) pilot plant.

Under the terms of agreements made in 1976 and in 1980, the Victorian Government through the Victorian Brown Coal Council is providing a serviced site at Morwell, coal supplies, and other assistance in environmental and plant operational matters. The Australian Federal Government also has assisted the project through foreign investment and import duty concessions, recognising the non-commercial nature of the pilot plant.

Figure 1 indicates the organisational structure concerned with the project.

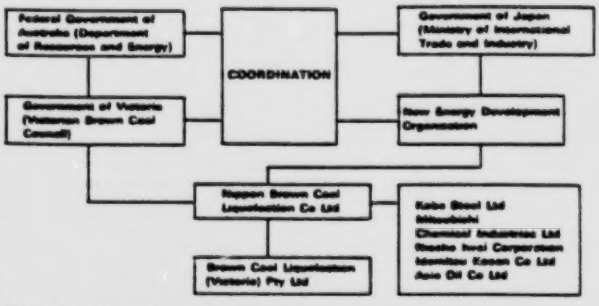

Fig 1 BCLV project organisational structure

Dr Kazuo Kunii is Managing Director of BCLV Pty Ltd. He previously worked at Kobe Steel Ltd, as Manager– Technical Department, Iron and Steel Division.

Dr Tetsuo Matsumura joined BCLV in 1983 as Manager– Technical Department. He spent 18 years in the Central Research Laboratory and 7 years in the Mechanical Engineering Laboratory of Kobe Steel Ltd.

Dr Ron Camier is Senior Engineer– Coal Corporation of Victoria. Prior to his present secondment to BCLV he worked for the Victorian Brown Coal Council, the State Electricity Commission of Victoria, and the CSIRO Division of Mineral Engineering.

The BCL process

The process being developed by NBCL for a commercial scale plant is based on the following components

- Raw brown coal having a moisture content of about 60% is dewatered, pulverised, and slurried with catalyst and recycle solvent. A particular feature of this step is an energy-efficient dewatering process which is integrated with the liquefaction process and recovers reusable water of industrial quality.
- In the primary hydrogenation section the brown coal is preheated and fed into high pressure reactors where the coal is liquefied to a relatively heavy product oil (ie SRC). Reaction conditions are in the range 430-460°C and 15-25MPa. An inexpensive, disposable catalyst is employed in suspended/entrained-bed type reactors.
- The used catalyst and mineral matter from the coal are removed from the heavy oil in a solvent deashing step which also is designed to optimise recycle solvent quality. The relatively low minerals and inorganics content of Victorian brown coal helps minimise oil losses in this step.
- The deashed product oil is then further hydrogenated to naphtha, middle distillate and fuel oil. Reaction conditions are in the range 360-450°C and 15-25MPa. This two-stage hydrogenation method employed achieves efficient consumption of hydrogen, and features catalytic fixed-bed type reactors in the second stage.
- The residue removed in the deashing step contains some carbonaceous material. This residue is gasified to provide the inplant fuel requirements of the process.
- The hydrogen gas required for the process is obtained primarily by steam reforming of the hydrocarbon off gases which are byproduced within the process.
- In addition to the previously noted self-sufficiency in recycle solvent, process cooling water, fuel gas and hydrogen; a commercial plant would also satisfy its own electricity and steam requirements by raw brown coal combustion.

The overall thermal efficiency of a commercial scale plant would be around 55%, comprising about 30% middle distillate and 25% naphtha yields. The process is shown schematically in figure 2.

The pilot plant at Morwell will consist of four main sections

(1) drying and slurrying
(2) primary hydrogenation
(3) solvent deashing
(4) secondary hydrogenation.

The former two sections will be completed by mid-1984 as Stage 1 of the program, and the latter two by early-1986 as Stage 2. Operation of Stage 1 and construction of Stage 2 will be concurrent. Also the new NBCL dewatering process will be tested as part of Stage 2. For the pilot plant only, natural gas will be used for process heating, and for hydrogen generation by steam reforming.

The output from Stage 1 will be about 30t/d of SRC and 5t/d of naphtha. In stage 2 the SRC is processed further to achieve a total yield of about 25t/d of middle distillate and naphtha.

Construction progress

Construction of Stage 1 began in November 1981, with an Australian construction management contractor, Davy McKee Pacific Pty Ltd being appointed. The work has proceeded remarkably smoothly despite an excessively hot summer in 1982/83 and some industrial relations delays in August 1983 and April 1984. Construction was substantially complete by June 1984, allowing commissioning to commence in parallel with the final stages of erection of other parts of the plant.

The earlier parts of the plant to be completed were the services sections such as the boiler, nitrogen and air supplies, water and wastewater treatment, sulphur recovery, compressors, laboratory, tank farm and gas holders. Subsequently the hydrogen generation, offgas treatment, coal preparation, slurry making, preheater and SRC solidification areas are being completed. The last sections to be completed will be the primary hydrogenation and distillation portions.

Table 1 presents a summary of the major equipment being installed in Stage 1, and their location is indicated by figure 3.

Table 1: Stage 1 main equipment specifications

Section	Input capacity
Coal preparation (crushing, screening)	50t/h
Raw coal drying	8.5t/h
Coal slurry making (ball mill, feed pump)	10t/h
Preheater and primary hydrogenation	8t/h
Hydrogen and recycle gas compression	10.000Nm³/h
Atmospheric distillation	3.7t/h
Vacuum distillation	8.3t/h
CLB solidifier (steel belt cooler)	2.1t/h
Acid gas removal (Benfield process)	800Nm³/h
Hydrogen generation (steam reforming)	3000Nm³/h
Hydrogen recovery (PSA molecular sieve)	1000Nm³/h
Sulphur recovery (Dismox/Claus/Minotaure)	1.4t/h
Tank yard	2400m³
Natural gas and offgas compression	3300Nm³/h
Boiler (natural gas fired)	24t/h
Nitrogen supply (liquid vaporisation, compression)	500Nm³
Air supply	1500Nm³/h
Water treatment	1800t/d
Cooling tower	1500t/h
Wastewater treatment	450t/d
Wastewater incineration	80t/d

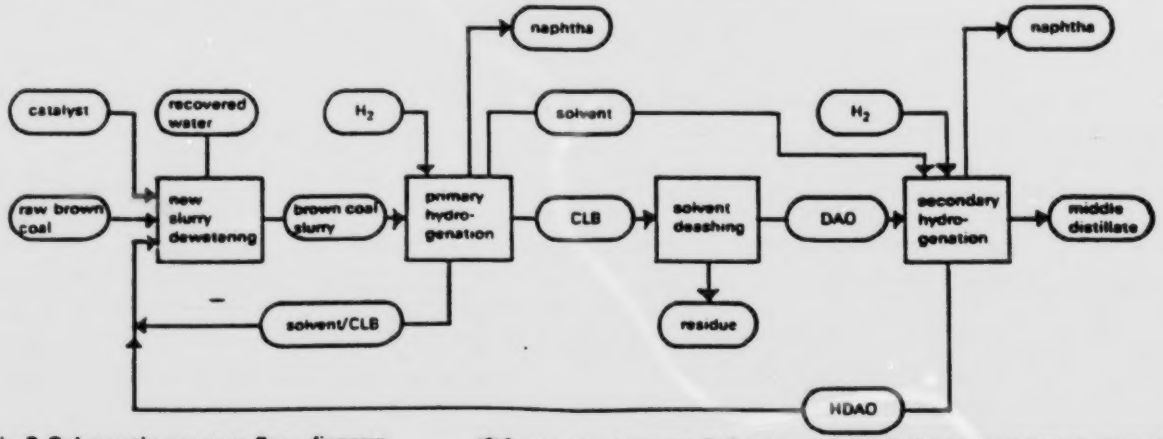

Fig 2 Schematic process flow diagram (CLB = coal liquid bottoms, DAO = de-ashed oil, HDAO = hydrogenated de-ashed oil).

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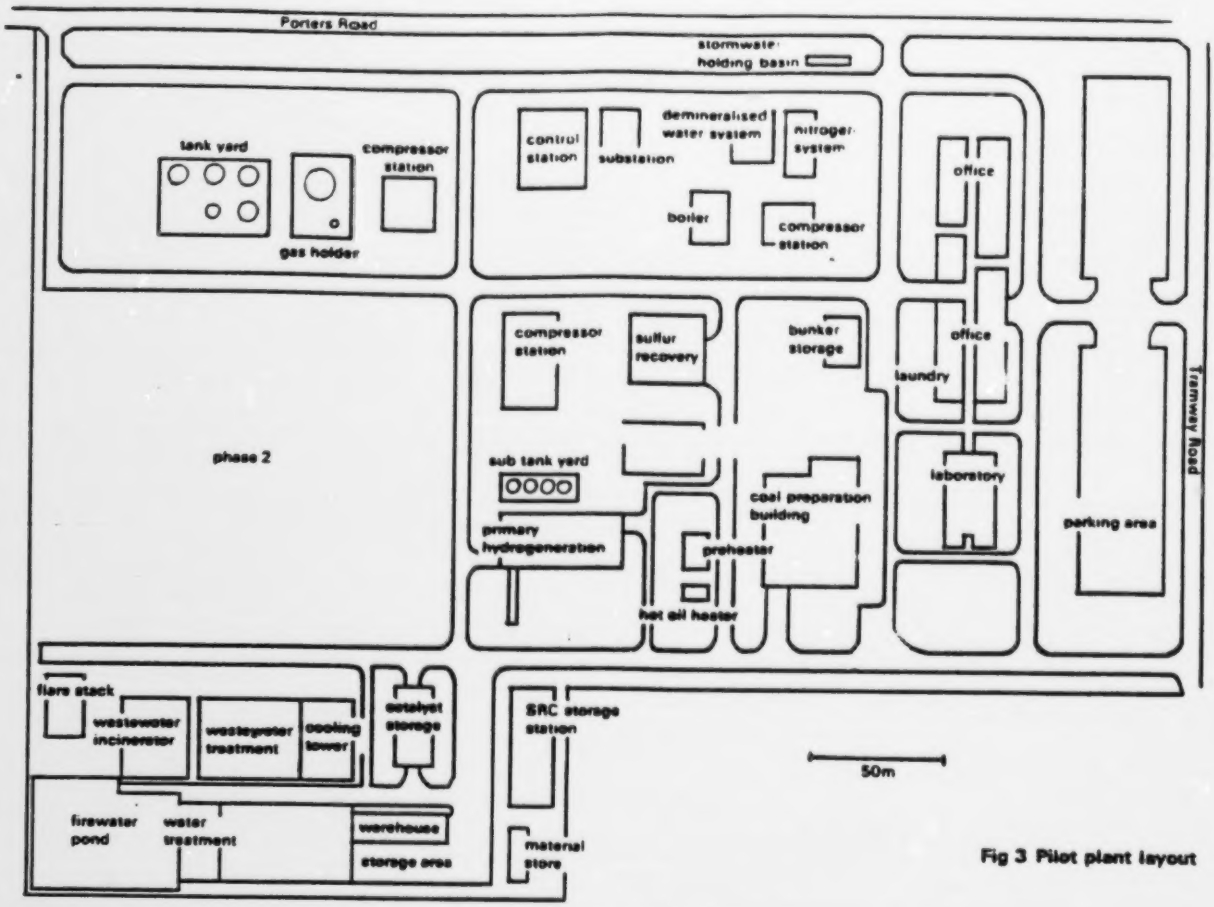


Fig 3 Pilot plant layout

For Stage 2 construction it will be necessary to apply methods which take account of the special conditions to be encountered, viz:

(1) The potential hazards of carrying out "hot works" (eg welding) adjacent to the already operating Stage 1.

(2) The limited remaining site area for contractor offices/amenities and equipment/materials lay down.

(3) The need to limit the Stage 2 construction period to coincide with the Stage 1 scheduled operation period, thereby avoiding unnecessary operational expenditure.

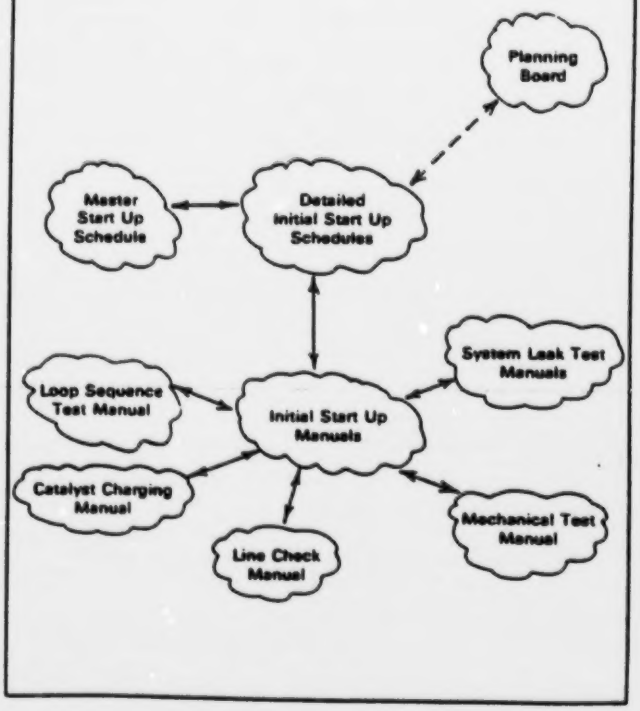
Appropriate methods are currently under consideration.

Commissioning of Stage 1

Commissioning of process units will take place progressively from mid-1984, as construction is completed. The services sections of the plant will be the first to be commissioned and the primary hydrogenation will be the last, similar to the sequence for construction completion. For most process units, commissioning consists of a leak/purge test using nitrogen, then a mechanical equipment test, followed by a test run of the unit. In the case of the primary hydrogenation section, the leak and mechanical tests are followed by about one month of nitrogen recycle testing at different temperatures and pressures. Then another month is spent on cold solvent recycle testing including emergency shutdown, after which another month is occupied with hot solvent recycle testing. Subsequently "coal in" will take place, and initial operation will be for the purpose of producing a brown-coal-derived equilibrium recycle solvent. For startup, a black-coal-derived anthracene oil will be used.

The documentation involved for plant commissioning is quite extensive, as is indicated by figure 4. The various

Fig 4 Documentation for commissioning



information sources shown are used to formulate the "Initial startup manuals". In summary, the commissioning documentation consists of the following:

(1) Master startup schedule
This single page schedule provides an overall summary of the startup plan, from which the critical path can be determined.

(2) Detailed initial startup schedules
These schedules are for individual plant sections. They form the main basis for writing the "Initial startup manuals", and are useful for reviewing commissioning interactions, and manpower and activity time allocations.

(3) System leak test manuals
These manuals give the general procedure for leak testing/purging with nitrogen. They include marked up P&IDs and data sheets for recording test conditions and results.

(4) Initial startup manuals
These manuals cover all procedures for commissioning each plant section, from construction handover through to normal operation, referring to the other commissioning documents as required.

(5) Loop sequence test manual
This manual includes trip/alarm/sequence logic diagrams for control loops and instrumentation, together with test methods and data recording sheets.

(6) Line check manual
This manual provides guidelines for precommissioning checks of systems for mechanical completion, process operability and operational safety aspects.

(7) Catalyst charging manual
This manual gives guidelines for charging the catalysts and resins used in the plant for eg hydrogen generation, sulphur recovery and water demineralisation.

(8) Mechanical test manual
This manual contains information required for testing specialised mechanical equipment: eg ball mill, drier and reciprocating compressors.

(9) Planning board
This is a pegboard type of visual aid constructed from the "Detailed initial startup schedules". It provides a flexible planning technique to indicate interconnections, and to coordinate commissioning activities.

Conclusion

The BCLV pilot plant represents a relatively large scale, long term experiment in a new technology. It will be the world's largest two stage direct hydrogenation pilot plant, and the only liquefaction pilot plant based on brown coal. However, just as importantly, it is also an experiment in the blending of Japanese and Australian cultures and working practices. Until now, this has been achieved satisfactorily, although not without some problems, through the construction and ongoing commissioning of the plant. These achievements augur well for the successful future implementation of the operational phase of the pilot plant.

Acknowledgements

The authors wish to acknowledge the assistance of NEDO, who funds the entire BCL process development, in granting permission to publish this paper. Thanks also are due to Messrs T. Oda and Y. Nakako of NBCL and J. Owen-Smith and P. Kennedy of BCLV for their helpful advice.

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The Coal Corporation of Victoria

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Summary

The Victorian Government will establish the Coal Corporation of Victoria as a commercially-oriented body to dynamically lead the development of the Victorian brown coal resource for alternative uses other than electricity generation.

Initially, at least, the new Corporation will be owned by the SEC but it will be at armslength and independent from the electricity business.

The Coal Corporation of Victoria will have its own Chairman and Board of six directors and report to the Minister. In appointing the Board, the Government will be seeking a significant representation from people with mining, resources and development backgrounds from the private sector and from the Latrobe Valley community as well as two nominations from the SEC.

Very speedy implementation will occur, and the Corporation will be quickly established during 1984. It will be able to draw on the knowledge, expertise, experience and activities of the SEC and the Victorian Brown Coal Council to accelerate its progress.

The new agency will be a commercial business and will be active and expert in providing advice and support to industry on brown coal, technical processes and options for early commercial application.

The SEC already has commercial operations for the production and sale of briquettes and brown coal to industry on a significant scale. The new Corporation will achieve immediate market presence and commercial identity, and financial self-sufficiency, by taking responsibility for the marketing and sales to the public and industry of briquettes and brown coal.

The agency will formulate a market development plan to be implemented with the private sector, including joint ventures. Known short-term to medium-term opportunities for briquettes, dried brown coal and solid carbon products will be actively promoted. Prospective longer-term opportunities such as solvent-refined coal, liquefaction of coal and synthetic natural gas will also be encouraged.

The focus of the coal winning aspect of the agency will be the central Latrobe Valley area where there are ample coal reserves to meet the coal commitments for power generation this century and into the next, together with substantial potential needs of private industry. Coal will be made available as appropriate from multiple end-use open cuts or from a dedicated open cut to be developed and operated for a specific end-user.

Operationally, the Coal Corporation of Victoria will enter into contracts with the electricity business for supply from existing open cuts developed for power generation purposes. The first such arrangements will cover at least five million tonnes annually from the Loy Yang open cut. It is proposed that at a later date the coal agency will become a coal winner, drawing on the world standard expertise within the SEC.

The new agency will submit its objectives, performance targets and financial estimates to the Minister as a separately identified business of the SEC. The agency will also be subject to a similar rigorous framework of accountability as that applying to the SEC.

The agency will be developed as a self-supporting business not requiring subsidies from either the Consolidated Fund of Victoria or from electricity customers. A cash flow base for the agency will be provided by the transfer of the existing SEC briquette business and brown coal sales whose gross sales currently amount to $22 million annually. For capital works financing, it is relevant that the SEC has a significant borrowing powers advantage in the market as a recognised borrower with a good credit rating and access as approved to the domestic and overseas markets. The appropriate financing option will also be influenced by potential end-user participation.

1 Introduction

On 9 April 1984 the Victorian Government announced the Economic Strategy for Victoria, which details economic initiatives and opportunities for the 1980s.

The Strategy emphasises that Victoria's extensive brown coal deposits constitute a key competitive strength for future economic development. It envisages that only by increasing economic activity in industries which utilise brown coal will the potential advantages of the brown coal resource be encapsulated in the Victorian economy for the employment and maximum benefit of all Victorians.

Government economic initiatives are therefore aimed at encouraging greater use of brown coal fired electricity production and, in addition, at improving opportunities for utilisation of brown coal and development of associated industries. These aims are to be achieved by suitably organising the management of the brown coal resource, providing access to low cost coal for the private sector, supporting research and development in brown coal for commercial applications, and promoting the active involvement of the private sector in commercial utilisation of the brown coal resource.

In the management of the brown coal resource, the Government has announced that:

- The SEC will continue to be responsible for the management, development and mining of all coal from its open cuts, and remain as an integrated coal-mining and electricity supply authority.
- Responsibility for the management, winning and co-ordination of the Victorian brown coal resource for alternative uses other than SEC power generation will be vested in an agency to be called the Coal Corporation of Victoria.
- The new agency will be owned by the SEC at least initially but will be at armslength and independent from the electricity business.
- The State will in the future seriously consider proposals to develop new coalfields for multiple end-users of coal. This will enable utilisation of the resource to fully benefit from economies of scale in coal production while permitting a controlled rate of development of the brown coal resource.

2 Functions

2.1 Principal Functions

The Coal Corporation of Victoria will encourage and support the active involvement of the private sector in achieving the commercial utilisation of the State's brown coal resources for uses other than electricity generation. Principal functions in this regard include:

1 Conduct and pursue a market research program to determine the potential for brown coal and brown coal products.

2 Promote the upgrading of brown coal into usable, convenient and commercial product forms by means of the active involvement of the private sector, including joint ventures.

3 Arrange the supply of brown coal from the Latrobe Valley to the private sector.

4 Undertake or arrange approved coal winning activities.

5 Involve the private sector in the promotion, marketing and distribution of brown coal and brown coal products world wide on a commercial basis.

6 Provide research and technical services to support process and product development and to expand fundamental understanding on brown coal. Co-ordinate public and private sector research and development programs and develop the Gippsland brown coal research laboratory.

7 Undertake resource planning for the portion of the brown coal resource not identified for electricity generation.

8 Promote State policies in relation to the efficient use of energy and resources, including the increased use and applications of brown coal.

Some important activities of the agency supporting the above principal functions will be—

- identification of companies with potential interest in utilising the coal resources;
- promotion of economic processes and negotiation with potential users on the quantity, quality and timing of their projected coal requirements;
- identification and promotion in conjunction with the SEC of opportunities for cogeneration in parallel with coal supply to new industries;
- identification, exploration and evaluation of the coal resources and reserves;
- development and implementation of relevant strategy plans;
- co-ordination with responsible authorities on appropriate land planning, acquisition and compensation, social services and infrastructure requirements;
- preparation and/or evaluation of specific commercial proposals for the utilisation of brown coal.

The functions for the coal agency are within the existing powers of the SEC and therefore the agency will be quickly established. However, amending legislation will prescribe that the Coal Corporation of Victoria will report separately to the Minister and submit its objectives, performance targets and financial estimates to the Minister. The entitlements of private users to coal vis-a-vis the electricity undertaking will also be covered.

2.2 Latrobe Valley Focus

The central Latrobe Valley area, with its very large, readily accessible coal resource and extensive development by the SEC, is distinguished from the balance of the Latrobe Valley, South Gippsland and the rest of the State. Major development other than in the central Latrobe Valley area is not expected until well into the next century. The focus of the coal winning aspects of the agency will therefore be the central Latrobe Valley area.

2.3 Commercial Emphasis

The new agency will be a commercial business. It will incorporate existing functions of the Victorian Brown Coal Council (VBCC) and of the SEC relevant to the agency's commercial operation.

The agency will be highly competent and active in providing advice and support to industry on brown coal, technical processes and options for early commercial application.

Immediate commercial identity and movement to self-sufficiency will be achieved by separating from the electricity supply business, the marketing and sales to the public and industry of briquettes and brown coal to provide a nucleus for commercial expansion by the agency.

Known market opportunities currently being developed by the SEC for briquettes and dried brown coal will be actively pursued, for example the cement industry, allied with appropriate investment by the agency. A dried brown coal pilot plant may be funded in conjunction with the National Energy Research, Development and Demonstration Council.

Following the call for registration of interest by parties wishing to utilise brown coal from a supply of at least 5 million tonnes per annum from the Loy Yang open cut, the new agency will gain quick insight into further possibilities for development through its discussions with companies interested in Loy Yang coal and by its access to overseas authorities and companies in this field. The agency will formulate a market development plan to be implemented by the agency with the private sector, including joint ventures.

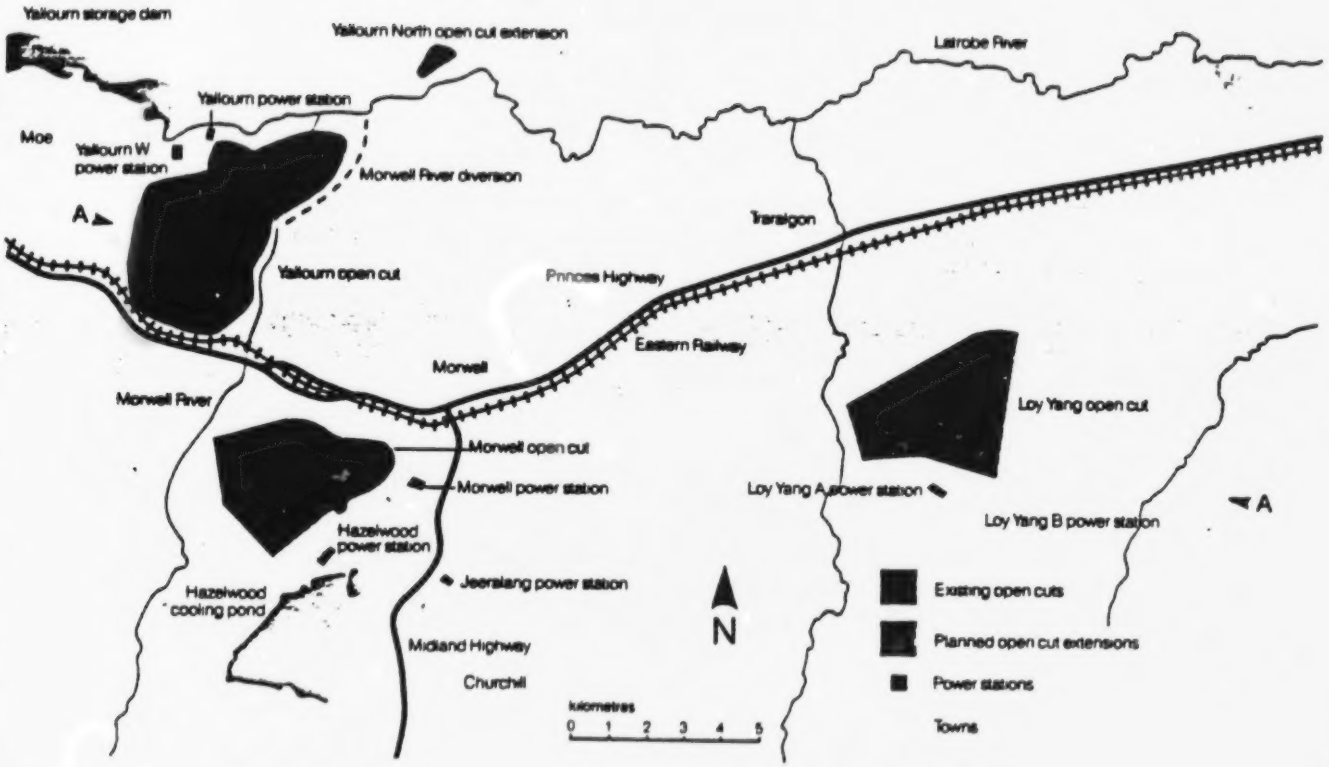
2.4 Research and Development

The four broad objectives in this area, as stated by Government are—

- upgrading brown coal to forms which are more convenient for transportation and combustion;
- ensuring that Victoria is well placed to take advantage of market developments or technical innovations as they occur;
- adapting conversion technology to the particular characteristics of the brown coal feedstock; and
- encouraging the production of higher value brown coal products.

These activities will place high emphasis on the realistic commercial opportunities, but longer-term possibilities must also be considered. It is essential that industry actively participate in and support research and development, although Government assistance is seen to be necessary for the continuation of basic brown coal research at this stage.

SEC
Latrobe Valley
Coalfield Development



Coal Seams in the Latrobe Valley

Section Through A-A

kilometres
0 2 4
Horizontal scale

metres
0 250 500
Vertical scale
Exaggeration 8:1

2.5 Resource Planning

The resource planning function involves advising and recommending on brown coal resource development matters to the Government through the Minister for Minerals and Energy or via the Ministerial Committee on the Latrobe Region. Close liaison will be maintained with the Latrobe Regional Commission (LRC).

Where strategy plans for open cut developments are approved by Government they will be passed to the LRC for incorporation into the Regional Strategy Plan. The agency will also advise and liaise with the LRC on the preparation of Infrastructure Co-ordination Plans for "Prescribed Developments" and provide details of coal winning works required for the annual preparation of the Co-ordinated Plan of Works in relation to major capital developments.

2.6 Coal Winning

The SEC has a world standard capability in planning, developing and operating open cuts. It will continue to be responsible for the management, development and mining of all coal from its open cuts. Customers of the coal agency will be able to have contracts for the supply of coal from these open cuts to ensure they receive reliable delivery against the arrangements negotiated.

It is proposed that the coal agency will become a coal winner, drawing on the world standard expertise within the SEC.

3 Organisation

The organisational arrangements involve establishing a discrete business under the Companies (Victoria) Code called the Coal Corporation of Victoria. Initially at least it will be owned by the SEC, but it will be at armslength and independent from the electricity business.

The new Corporation will have its own Chairman and Board of six, with significant representation of people with resources, mining and development backgrounds in the private sector and from the Latrobe Region community. Two only will be Commissioners from the Board of the SEC.

This structure will ensure that the interests of the agency are not subservient to the electricity side of the SEC but that the new Corporation has proper access to the knowledge, expertise, experience and activities of the SEC as well as the Victorian Brown Coal Council, the functions of which will be incorporated into the Corporation.

The agency will—

- act in a commercial manner;
- be responsible and accountable as a separate business, but within the terms of the SEC Act;
- have the expertise to fulfil its functions for the maximum benefit of the State; and
- be capable of expansion as business activities develop.

Supporting the Chief Executive Officer of the agency will be a General Manager controlling three management functions of—

1 Marketing

2 Resources and Production

3 Development Services

Briquettes will be a discrete business activity.

Staffing of these functions will be kept tight, supported by contract/consultant assistance from the SEC and other organisations. Initial staffing will be achieved by the transfer of relevant SEC and VBCC personnel with some external recruitment. The new Corporation will comprise some 80 personnel initially, including about a dozen relocated to the Latrobe Region.

The Corporation head office will be in the Latrobe Valley with a commercial bureau in Melbourne.

4 Finance

The agency will be developed as a self-supporting business not requiring subsidies from either the Consolidated Fund of Victoria or from electricity customers.

A cash flow base to the agency will be provided through the existing SEC briquette business and brown coal sales. The accounts of the SEC electricity business and of the agency business will be arranged accordingly.

At present the SEC total annual sales of briquettes and brown coal amount to some 520 kt and 230 kt respectively, with gross sales revenue around $22 million. Strong growth potential exists to increase sales of both briquettes and brown coal to the public through entrepreneurial marketing and pricing strategies. Its revenues will be expanded by the Loy Yang coal sales to the private sector which the Corporation will handle.

The agency's cash outflows will arise from five broad sources:

- Marketing
- Production
- Development Services
- Management and Administration
- Capital Works

Marketing and production costs will initially be associated with the briquette business and brown coal sales and the establishment of new markets.

Development services include: programs involving ongoing basic research into brown coal properties; and programs involving the development of potential commercial applications and technologies.

Ongoing basic research is an activity which involves the extension of knowledge on the properties of brown coal and should be regarded as a long-term investment in the economic well being of Victoria. It is proposed therefore that the annual cost of ongoing basic research be met by Government as an annual grant.

Programs involving potential commercial applications and technologies will be financed jointly by the agency and the commercial parties who will benefit from the outcome of the research. The agency will therefore encourage research and development on potential commercial applications and technologies by the private sector. To the extent possible the outcomes from development programs will be made available on a commercial basis.

Management and administrative costs, including costs associated with resource planning, will be strictly controlled and be met by the agency from its sales revenue.

Capital works such as those associated with new open cuts or extensions to existing open cuts, land acquisition and infrastructure, coal winning, storage and distribution facilities will require financing ahead of actual sales revenue. To establish the appropriate source of finance, alternatives would need to be evaluated in light of the actual investment proposed. Such options would include—

- long-term loan raising from domestic and offshore capital markets (the SEC has a significant borrowing powers advantage as a recognised borrower with a good credit rating and access to the domestic and overseas markets as approved);
- long-term loans from Victorian Development Fund;
- equity participation by external parties; and
- sale and lease back arrangements.

The final selection of the appropriate financing source will be influenced by potential end user participation and by the relative advantages to each party, particularly if a joint venture is possible.

The agency will submit its objectives, performance targets, and financial estimates to the Minister as a separately identified business of the SEC.

Similarly, the financial policies and procedures and cost controls now in place in the SEC will be implemented within the agency. It will be subject to a similar rigorous framework of accountability as that applying to the SEC.

The economic benefits to the State will accrue through a dividend on equity in a similar manner to that applied to the SEC electricity business. Investment in future coal developments by both the public and private sector will increase economic activity and enhance employment opportunities and the involvement of the private sector in production operation will generate additional revenue through appropriate State taxes and charges.

5 End-use development

5.1 Projected New Demands

The projected new demands for brown coal in the short-term to medium-term include:

- **Dried Brown Coal**

Dried brown coal, primarily for industrial boilers, cement kilns and auxiliary fuel for power generation will permit coal to substitute for natural gas and oil.

With increasing economic and resource pressures there are a number of new initiatives emerging for the production and use of dried brown coal (DBC). Already consideration has been given to the logistics and economics of supplying DBC from the Morwell Briquette Factory to cement manufacturers in Geelong.

The studies currently being undertaken by the VBCC on market opportunities for DBC and on drying technologies appropriate for further development, will provide a valuable consolidation of information in this area.

Recognising its own needs for a briquette substitute as an auxiliary fuel for power generation, the SEC has undertaken research and development on production of lump DBC through the solar drying of slurried coal. This product could have significance in applications beyond the power industry. The process has been investigated over the range from fundamental coal chemistry to 100 kg batch trials and a proposal has been detailed for a pilot-scale development program to establish the commercial basis for the process. Federal Government support for this pilot plan is being sought through the National Energy Research, Development and Demonstration Program.

Other processes, such as the Evans-Siemon thermal dewatering process and its equivalents, have the potential to extend the brown coal resource significantly due to their higher thermal efficiencies. These processes have been investigated experimentally and their practicability is being continuously monitored. In this context the SEC has past experience with kiln drying and direct contact steam drying of brown coal, in addition to the technologies of steam-drum drying and mill drying currently applied in the briquette factories and power stations.

- **Solid Carbon Products**

Solid carbon products for use as reductants in specialised processes, and as anode and activated carbons are areas in which there are good prospects for further commercial application.

In the past the SEC has provided considerable technical support and assistance in relation to the establishment of the unique processes operated by Australian Portland Cement Ltd in Traralgon and Australian Char Pty Ltd in Morwell. Both of these operations demonstrate the type of support for commercially independent applications that can be provided.

The SEC has had interactive contact at several levels with entrepreneurial organisations having interests in the development of special forms of carbon from brown coal: the manufacture of anode carbons and of activated carbons are two examples. A detailed knowledge of coal chemistry, inorganic constituents and the variability characteristics of the Latrobe Valley coals has been established by the SEC's Herman Research Laboratory. This scientific understanding is a most valuable basis for further development towards the production of special carbons.

A particular characteristic of some Latrobe Valley brown coals is the very low level of contamination by minerals. The understanding of this and other chemical characteristics of these coals provides prospect for the production of relatively pure industrial carbons through the adaptation of existing technologies.

In the longer-term there are prospective developments that could increase demand for brown coal, namely:

- **Solvent Refined Coal**

The application is as a synthetic additive to control the characteristics of blends of coal for the production of metallurgical coke, or as a precursor for other carbons such as fibres for reinforced plastics.

- **Liquefaction of Coal**

The SEC is suppying coal for the operation of the BCLV pilot plant at Morwell. Continued and close involvement with developments in this area will be a major requirement for the agency.

- **Synthetic Natural Gas**

  While it is unlikely that this development would be required for reticulated gas until well into the next century, there are active developments in technology proceeding overseas. The SEC has long-term interests in the use of coal for power generation, and gasification could be required as the primary process for energy conversion in high efficiency cycles.

5.2 Coal Supply

The estimation of reserves of coal needed for future power generation depends upon long-term forecasts of electricity demand. However, there are ample reserves of coal in the western coalfields of Morwell, Driffield and Maryvale and in the Loy Yang area to meet the coal commitments for power generation this century and into the next until at least the year 2010. For the most likely scenario, some 2000 million tonnes of coal is potentially available to the private sector from present and projected open cuts including about 300 million tonnes and 100 million tonnes from the existing Loy Yang and Morwell open cuts, respectively.

The considerable cost and long lead time required to develop new coalfields means that new open cuts would generally need to serve multiple end users of coal. However, in the event of a process being established on a large scale it would be appropriate for a dedicated open cut to be developed and operated for a specific end user.

Whatever the arrangements for open cut development and operation, close liaison and co-ordination over many technical areas will be essential.

Within the confined area of the central Latrobe Valley, technical considerations including artesian dewatering, open cut developments and associated earth movements, overburden disposal and river diversions affect areas well outside the boundaries of individual open cuts. These aspects must be considered in respect of SEC power generation requirements and requirements for other uses before new projects are undertaken so that mutual impacts of coal winning operations are fully considered; also to ensure that development of the total brown coal resource is in accordance with the Victorian Energy Plan and Economic Strategy.

The allocation of coal and sequencing of coalfield development is an ongoing Government policy issue on which the Government will receive advice from the Department of Minerals and Energy.

5.3 Development Services

The SEC already has well developed facilities and expertise to support research and provide technical services for the commercial utilisation of brown coal.

The coal laboratory at the Gippsland Institute will be effectively incorporated into the agency, including working in tandem and interchanging staff with the Herman Research Laboratory. The expansion of the Coal Corporation of Victoria's research and development and technical support will be accomplished at the Gippsland coal laboratory.

The SEC's Herman Research Laboratory has developed as an integral part of the Commission's activities and is essential to its operations. It is a major laboratory of world standing, conducting research directed primarily at improving generation, transmission and distribution of electricity in the planning, design, construction, commissioning and operational phases. The work ranges from basic applied research through development and demonstration to establishing the application in practice. Both innovative and development research are undertaken. The emphasis is on the use of brown coal.

The existence of these extensive facilities and the established expertise has provided the opportunity for work in related areas to be done, with the immediate application of advanced and sophisticated research techniques.

FORTUNE THE FUTURE

Loy Yang coal properties and utilisation characteristics

The Government of Victoria has identified the abundant brown coal of the Latrobe Valley as a major element in the strategy for enhancing the State's economic future. It is actively encouraging the development of brown coal based industries.

The Coal Corporation of Victoria is able to supply brown coal to private industry. Five million tonnes per year is available from the Loy Yang open cut and this coal is probably the lowest cost, high purity, organic carbon feedstock available in commercial quantities in the world.

The purpose of this statement is to summarise the present understanding of the properties and utilisation characteristics of Loy Yang coal.

Properties

Geological setting

The Loy Yang coalfield is located south-east of Traralgon and within the Latrobe Valley Depression of the Gippsland Basin. Three groups of major coal seams formed in this area. The oldest coal seams belong to the Traralgon Formation and are overlain by the complex system of thick seams of the Morwell Formation. The youngest coal seam forms part of the Yallourn Formation.

In Miocene/Pliocene times the once essentially horizontal sediments were tilted, folded and locally faulted. Widespread erosion followed and removed substantial volumes of coal from uplifted blocks. As a result, in some areas thick coal seams were left at shallow depths, whereas coal in adjoining areas was either partly or completely eroded or depressed to considerable depths.

The dominant structure of the Loy Yang coalfield is the closed Loy Yang Dome. The Loy Yang open cut is located on the northern slope of the Loy Yang Dome with beds showing a general 4 to 8 degrees dip in a northerly direction. Successively younger coal seams sub-crop towards the north beneath a shallow cover of overburden and are separated by thin interseam sediments.

A plan of the Loy Yang open cut is shown in Figure 1. Geological sections of the area showing location of the seams are given in Figure 2. The coal to be mined comes almost entirely from the Morwell Formation, comprising the Morwell 1A, 1B and 2 seams.

Mining has commenced on the southern boundary of the open cut where the lowest (Morwell 2) seam sub-crops and will develop northwards, reaching a depth of some 200 metres along its northern margin. The cut will then be developed eastwards and southwards to terminate on the southern boundary. The coal will be taken mainly from the Morwell 2 (400 million tonnes) and Morwell 1B (600 million tonnes) seams with a relatively small quantity from the Morwell 1A (70 million tonnes) seam. The seams vary in maximum thickness between 40 and 90 metres, with interseam sediments up to 15 metres thick. Overburden material varies between about 8 and 25 metres thick.

The amount of coal planned to be won is about 1000 million tonnes but there is scope for increased production by up to 300 million tonnes.

Chemical properties

The coal has been extensively surveyed with bores drilled on a 400 metre grid over the open cut and surrounding areas. Coal compositions and properties have been obtained from analysis of these bore hole samples and a comprehensive data base assembled, from which these assessments of coal quality have been made.

Loy Yang coal is typical of Latrobe Valley brown coals, having high moisture content and low levels of inorganic constituents.

The weighted average and distribution of moisture, ash, specific energy and the main constituents of coal over the whole open cut are given in Table 1. There is little variation in rank of the coal between the three main seams to be won – each has average moisture and specific energy close to the open cut average. Variation in properties with coal type (lithotype) occurs within seams. The lithotypes occur as distinct bands which can be correlated over large distances between bores.

Table 1

Loy Yang coal analysis
Analysis of bore hole samples,
Loy Yang open cut

ITEM	WEIGHTED AVERAGE (all coal seams)	CUMULATIVE FREQUENCY DISTRIBUTION 5%	50%	95%
Moisture (% wb)	62.7	59.2	62.7	65.9
Ash (% db)	1.4	0.8	1.2	3.9
Volatile Matter (% db)	51.4	49.1	51.6	54.3
Carbon (% db)	68.4	65.6	68.8	70.7
Hydrogen (% db)	4.9	4.6	4.9	5.2
Nitrogen (% db)	0.5	0.4	0.5	0.6
Sulphur (% db)	0.4	0.2	0.3	0.7
Oxygen (% db) (by difference)	24.3	Not available		
Specific Energy, MJ/kg				
Gross Dry	26.6	25.1	26.7	27.8
Net Wet	8.0	6.9	8.0	9.1

wb - wet basis db - dry basis

The weighted average and distribution of the main inorganic constituents in the coal are given in Table 2. These constituents are expressed as oxides and elements. Those expressed as oxides are usually present in the form of discrete minerals (e.g. quartz, clay and pyrite/marcasite). Those expressed as elements are predominantly present as carboxylates and dissolved salts in the coal.

Table 2

Loy Yang coal inorganic constituents
Analysis of bore hole samples,
Loy Yang open cut

CONSTITUENT (% Coal db)	WEIGHTED AVERAGE (all coal) seams)	CUMULATIVE FREQUENCY DISTRIBUTION 5%	50%	95%
Silica (SiO_2)	0.34	0.02	0.10	1.41
Alumina (Al_2O_3)	0.38	0.02	0.16	1.32
Potassium Oxide (K_2O)	trace			
Titanium Dioxide (TiO_2)	trace			
Pyrite/Marcasite (FeS_2)	trace			
Iron (Total) (Fe)	0.13	0.05	0.12	0.25
Calcium (Ca)	0.04	0.01	0.03	0.12
Magnesium (Mg)	0.08	0.03	0.06	0.17
Sodium (Na)	0.11	0.04	0.08	0.33
Chlorine (Cl)	0.14	0.05	0.10	0.37

Aluminium also occurs in an acid-soluble form in Loy Yang coals and strongly influences ash characteristics.

Ash formed from the combustion of this coal will consist mainly of oxides of the above elements, together with some sulphur retained as sulphate and small amounts of chloride.

On average the levels of inorganic constituents in the coal are very low. This is particularly the case for the mineral species. The concentration of the individual inorganic constituents varies both horizontally and vertically within the open cut and is not generally related to coal seam. Mineral species are mainly concentrated at the top and bottom of seams, as a result of contamination by the overburden and interseam sediments.

The inorganic elements, not occurring as minerals but being bonded to the organic coal fraction, are more uniformly distributed through the field. There is still considerable variation with position and depth, but this is not related to seam boundaries.

The inorganic elements sodium and chlorine are the most abundant of the non-mineral species, predominantly occurring as sodium chloride dissolved in the water associated with the coal. Highest levels are found at the top of coal, decreasing rapidly with depth. Higher sodium chloride levels are confined to limited areas of the open cut; the bulk of the coal has low levels of all inorganic elements.

Physical properties

Loy Yang coal is a soft brown coal and has a well developed pore structure which is filled with water in the natural state. The coal has high porosity and surface area, and undergoes considerable shrinkage on drying. Table 3 lists physical properties of the coal obtained from tests on raw and dried samples of coal taken from bore holes in the open cut area.

The variations in physical properties have generally been found to correlate well with a colour index, suggesting that the variation is mainly dependent on coal type (lithotype).

The bed moist coal has a specific gravity of about 1.13, but with breakage during mining the bulk density of run-of-mine coal is expected to be about 750 kg/m^3. Run-of-mine coal may have lumps of nominal diameter up to 0.5 metre.

The equilibrium moisture content of air-dried coal is approximately 15 per cent.

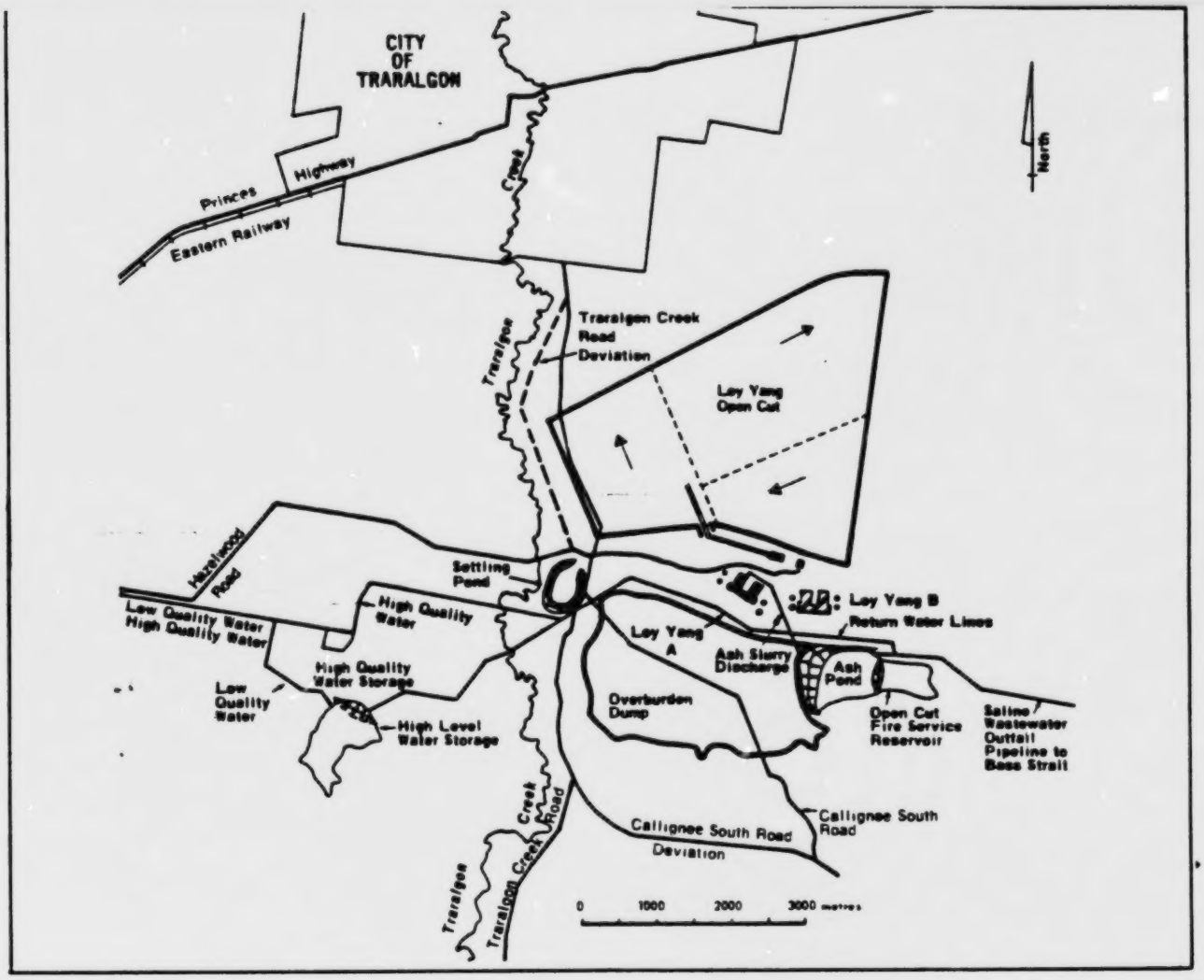


Figure 1: General layout of the Loy Yang Project, showing the Loy Yang open cut.

Table 3

Loy Yang coal physical properties Measured on test bore samples, Loy Yang open cut

PROPERTY	WEIGHTED* AVERAGE	RANGE
Porosity, percent	43.9	25.1 – 50.6
Surface area, m^2/g	263	186 – 305
Helium (true) density, g/cm^3	1.428	1.365 – 1.468
Mercury (apparent) density, g/cm^3	0.800	0.688 – 1.062
Air-dried coal specific gravity	0.738	0.649 – 0.941
Raw coal density, g/cm^3	1.129	1.106 – 1.156
Moist coal specific gravity	1.131	1.121 – 1.147
Shrinkage (air dried), percent	29.7	16.9 – 49.4

*based on 30 samples taken from three test bores within the boundaries of the Loy Yang open cut. The weighted averages were calculated using the proportion of coal types (lithotypes) as the weighting factors.

Utilisation characteristics

Loy Yang coal is presently used to produce electricity by direct combustion in a thermal power station. Its suitability for this purpose and its likely behaviour in the various aspects of the process have been thoroughly investigated by the SEC in a range of laboratory and pilot scale studies over many years. Thus its combustion behaviour and the characteristics of its combustion products are now well understood.

Together with other Latrobe Valley coals, it has also been tested to determine its suitability for other uses and processing into a wide range of alternative products.

Drying

Raw brown coal has its pore structure filled with water. Most of this water is not chemically combined with the coal but is readily removed by evaporation. The rate of drying down to the equilibrium moisture content (about 15 per cent) is governed by the rate that heat can be transferred into the coal. At equilibrium with ambient air, moisture corresponds to a layer one or two molecules thick on the internal and external surface of the coal. The drying behaviour of Loy Yang coal is similar to other high-moisture brown coals.

Dewatering

Thermal dewatering reduces the moisture content of brown coals by non-evaporative drying. In the process, bed moist coal is heated to temperatures of 250°C - 300°C in a vessel maintained at pressure above the saturated steam pressure to prevent evaporation of water from the coal. During this treatment, chemical and physical changes occur in the coal which result in the loss, as a liquid, of about three-quarters of the moisture in the coal.

A major advantage of this method of drying is the much lower energy requirement compared with conventional evaporative drying. A significant added advantage is the removal of much of the troublesome water-soluble sodium chloride in the separated liquid.

Experiments conducted on Yalloum, Morwell and Loy Yang coals showed that dewatering reduces the moisture content to about 30 per cent without any evaporative contribution. The degree of dewatering achieved increases with temperature. The bulk of the change takes place in the first few minutes after reaction temperature is reached, and temperatures above 250°C are needed to produce significant effects.

In these experiments, the Loy Yang samples were found to dewater better than the other coals.

Briquetting

The technology of drying and briquetting brown coal to produce hard lump coal is well established. Yallourn open cut coal has been briquetted for over 60 years, but Morwell open cut coal has not been successfully briquetted commercially.

No significant problems were experienced in producing high quality briquettes when a bulk sample of Loy Yang coal was processed at the Morwell Briquette Factory in 1975. These briquettes had both good strength and good weathering characteristics.

Petrographic studies and experience suggest that the darker lithotype coals in the Latrobe Valley are less satisfactory for briquetting. Loy Yang coal has a relatively low proportion of darker lithotypes, and, on this basis, may be particularly suitable for briquetting.

Solar dried brown coal slurry (SDBCS)

The solar drying of slurried brown coal is a process which produces a dry, high density, storeable lump coal.

Raw coal (60 percent moisture) is mixed with water in the ratio of about three parts to one of water and is milled to form a very fine, concentrated non-settling suspension. This material is then poured into ponds to a suitable depth and is allowed to dry by evaporation.

As moisture evaporates, the slurry shrinks and cracks to form homogeneous lumps. At equilibrium moisture content this material is hard and dense and has similar properties to those of brown coal briquettes. It can be harvested, stockpiled and used in the same way as briquettes.

The key to the SDBCS process is the particle size reduction in the slurry milling stage. This destroys most of the macroporous structure of the coal and produces a slurry with a polydisperse particle size distribution with a maximum packing fraction of about 75 per cent. The properties of the product improve as the slurry particle size decreases towards a median particle size in the range 8 to 10 microns. Laboratory and small scale tests have demonstrated that the SDBCS process is technically viable as well as being commercially attractive. A large pilot-demonstration plant is planned. Federal Government support for this pilot plant is being sought through the National Energy Research, Development and Demonstration Program.

Milling and grinding

Milling of raw brown coal is carried out in practice in a fan or hammer mill, usually in conjunction with hot gas drying. Investigations of this combined process show that most of the drying occurs after size reduction. Loy Yang coal is successfully milled by this process, having similar characteristics to other soft brown coals.

Dried brown coal can be ground in hammer or bowl mills. Samples of air-dried Loy Yang coal have been tested for grindability (Hardgrove Index). Hardgrove Indices ranged from 104 to 180, being rated from soft to very soft.

Briquetted coal is much harder than dried coal. Yallourn coal briquettes have a Hardgrove Index of about 55 with a range of 45 to 75. The Hardgrove Index of the Loy Yang coal briquettes produced in 1975 was measured at 54. It is expected that the range would be similar to that found with Yallourn coal.

Ignition and combustion

Ignition and combustion of brown coal particles involves four sequential and partially overlapping stages of drying, particle heating, devolatilisation and char burning. Loy Yang coal has a high volatile matter content and high temperature devolatilisation experiments conducted by the British Coal Utilisation Research Association (BCURA) showed that these samples of brown coal decomposed as fast as, and sometimes faster than, any British swelling coal. Most of the volatile material determined in brown coal analysis is non-hydrocarbon compounds (CO_2, H_2O, CO). The tar yield is about 12%.

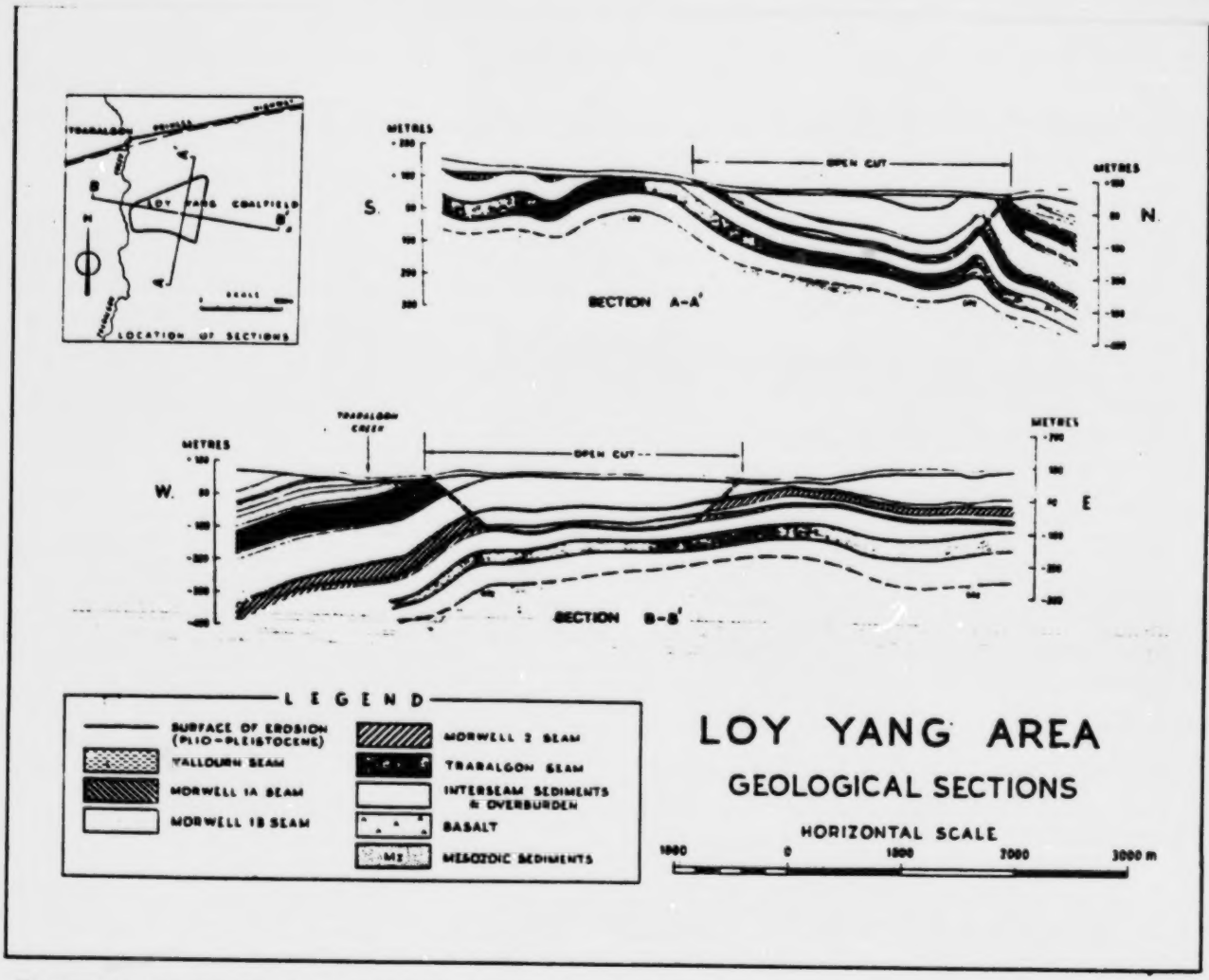


Figure 2: Geological sections through the Loy Yang area, showing coal seams and the location of the open cut.

Combustion experiments on devolatilised coal (char) particles of Loy Yang coal have been conducted by both BCURA and the Commonwealth Scientific and Industrial Research Organisation (CSIRO). These found that the combustion rate at elevated temperatures was very high and essentially limited by the rate of diffusion of oxygen to the surface of the coal particles. Latrobe Valley brown coals have very high internal surface areas, giving reaction rates that are much greater than for high rank coals.

Ignition and combustion behaviour of brown coal is strongly dependent on the combustion system in which it is used. In direct firing systems for raw coal, the drying gas and the moisture from the coal are included with the burner stream, affecting the aerodynamic and thermal characteristics of the burner system. Thus, raw coal moisture content is an important factor affecting burner design and performance.

In dried coal combustion, moisture does not limit thermal characteristics and Loy Yang coal is easy to ignite and burn in conventional burner systems.

Ash fouling and slagging

Ash fouling and slagging of heat transfer surfaces in combustion systems has a significant effect on design and operation because of the reduction in heat transfer capability of the surfaces. Loy Yang coal generally has low levels of inorganic constituents but, unlike most other coals, a high proportion of the ash-forming constituents are present in the coal as carboxylate salts which include iron, calcium, magnesium and sodium. In some parts of the open cut, aluminium also occurs in the coal in an acid-soluble form.

Ash formed from the combustion of this coal contains mineral particles, oxides of the above elements plus some sulphate and small amounts of chloride. The tendency for the ash to accumulate on heat transfer surfaces as bonded deposits or slags depends on the relative proportions of the various inorganic constituents.

Sodium is particularly important, since sodium species can exist as vapour at combustion temperatures and can diffuse into cooled ash deposits and react to form complex sulphates

which bond ash particles together. Sodium can also combine with silica and alumina to produce low melting point mixtures that can form slags in uncooled or overheated ash deposits.

Generally, the low levels of inorganic constituents in Loy Yang coal suggest that ash fouling and slagging will be low and combustion tests confirm this. However, there are some parts of the open cut where high sodium contents are found in the upper levels of coal, and significant fouling could occur with this coal. Slagging could also occur if silica were present as can happen with coal close to the overburden.

Another inorganic constituent which can significantly affect ash behaviour is aluminium when it occurs in an acid-soluble form as distinct from being present as a constituent of clay (mineral) inclusions. On combustion the acid-soluble aluminium forms alumina particles having high surface area and low bulk density. These particles appear capable of adsorbing sodium and rendering it less able to react with other ash particles to form deposits or slags. Significant quantities of acid-soluble aluminium occur at Loy Yang adjacent to overburden and interseam sediments. This coal should form weak deposits even if sodium is moderately high, but these deposits will require frequent removal to reduce their effect on heat transfer.

The likely ash fouling behaviour and its variation within the open cut area is still being actively investigated.

Because most of the inorganic material is in an ionic form in the coal, the ash nature will depend on the thermal history of the combustion process. There is some evidence that high combustion temperatures will produce ashes that are more likely to cause fouling. This needs to be taken into account when considering combustion of dried coal.

Combustion-generated emissions

Nitrogen Oxides: Power station emissions of NO_x result from two sources; oxidation of nitrogen in the coal and oxidation of atmospheric nitrogen, both reactions occurring in the flame zone. With brown coal combustion systems presently used, temperatures are low and atmospheric nitrogen makes a relatively small contribution to NO_x emissions.

The proportion of fuel-nitrogen converted to NO_x depends upon the temperature and stoichiometric sequence undergone by the coal during combustion, and NO_x reduction techniques based on control of combustion conditions have been developed. Loy Yang coal has low nitrogen content by world standards (0.5 per cent dry basis) and pilot scale tests conducted in the USA have shown that Loy Yang coal will produce very low NO_x emissions when burned in current low-NO_x combustion systems.

Sulphur Oxides: Loy Yang coal also has low sulphur content by world standards (0.4 per cent dry basis) and in addition, part of the sulphur in the coal is retained as sulphate in the fly ash. The extent of sulphur retention depends on the level of sodium, calcium and magnesium in the coal and the thermal and concentration history through the combustion system. In general, sulphur emissions from combustion of Loy Yang coal should be low.

Chlorides: Most of the chlorine in Loy Yang coal is present as sodium chloride. To the extent that the sodium is sulphated, chlorine will be released to the flue gas as hydrogen chloride. Normally all the chlorine will be released. Hydrogen chloride emissions will be low except where sodium chloride is high.

Particulates: The quantity of fly ash produced from Loy Yang coal will be low, and in general it will be easy to precipitate. This has been demonstrated in pilot precipitator tests. However, those Loy Yang coals which have high levels of acid-soluble aluminium will produce ashes which are difficult to remove from the flue gas. This is because these ashes have very low bulk density and, although efficiently collected onto precipitator plates, are readily re-entrained into the gas stream when the plates are rapped.

Carbonisation

High temperature char is usually produced by carbonising brown coal briquettes at about 800°C in a semi-continuous vertical retort. The objective is to provide a high strength lump char for metallurgical and other process applications and the tar is regarded as a by-product. A good indication of the yield of char from brown coals can be obtained from the proximate analysis, which is performed at 900°C. The volatile analysis, content of Loy Yang coal is about 51 per cent, indicating a char yield of about 49 per cent on a dry coal basis.

Strength and abradability characteristics of the char depend upon the quality of the briquettes and process variables such as temperature profile down the retort. Technologists from the German Democratic Republic (GDR) have also established that char quality is influenced by coal petrography. Based on petrographic criteria, Loy Yang coal appears particularly suitable for high temperature carbonisation.

The generally low levels of inorganic constituents in Loy Yang coal suggest it would be most suitable for char to be used as a carbon feedstock for metallurgical and chemical processes and for production of active carbon.

Tar production

Tar for use as a feedstock for liquid fuel and chemical production can be produced by low temperature carbonisation or by flash pyrolysis. Much experience with production and use of tar by low temperature (600°C) carbonisation is available in the GDR where a 12 per cent tar

yield is regarded as the minimum viable limit. Work conducted on Latrobe Valley coals showed that about half the samples tested were likely to have tar yields greater than 12 per cent. The lighter lithotypes were found to give the best yields.

Flash pyrolysis is a new technology for obtaining enhanced tar yields by rapidly heating coal particles in an entrainment or fluid bed reactor. Research on this technique has been conducted by CSIRO with laboratory-scale studies and process development rigs. The tests covered a range of coals. Tar yields up to 23 per cent were obtained for Loy Yang coal, close to the yields obtained for bituminous and sub-bituminous coals. This good performance occurred because of the low level of inorganic ions present as carboxylate salts in that particular Loy Yang coal sample.

Liquefaction

Brown coal is regarded as a very good prospect for liquefaction via direct hydrogenation and considerable research has been conducted to establish hydrogenation reactivity and relative hydrogenation performance of Victorian brown coals. As a result of batch autoclave studies conducted by the Victorian Brown Coal Council, it can now be said that all the Victorian brown coals tested are suitable as feedstocks for further testing at pilot plant level. In these tests overall conversions to liquid and gaseous products, often in excess of 90 per cent, were obtained and net liquid yields of 50 per cent were not uncommon.

Further liquefaction tests on Morwell coal have been conducted under continuous processing conditions, both in the CO-Steam (with carbon monoxide and steam) mode by Australian Coal Industry Research Laboratories (ACIRL) and in the more conventional hydrogenation mode by BHP Melbourne Research Laboratories.

The BHP test program included a sample of coal from a location just to the east of the Loy Yang open cut. This coal caused few operational problems and produced good yields of liquid products.

Although coal from the Loy Yang field has only been tested in small-scale laboratory reactors, Morwell brown coal has been successfully liquefied in pilot plants in Japan and West Germany.

A feature frequently encountered during hydrogenation of low rank coal is the formation of carbonate deposits in the reactors. Such problems have occurred during the hydrogenation of Morwell coal, due primarily to its relatively high level of ion-exchangeable calcium and magnesium. Loy Yang coal has low levels of these cations (Ca plus Mg total approximately 0.1 per cent, dry basis) and no significant carbonate formation has been observed in laboratory scale tests.

Loy Yang coal is particularly suitable for liquefaction via hydrogenation, due to its high reactivity, low level of ash-forming constituents (particularly Ca and Mg) and relatively low levels of sulphur and nitrogen.

Gasification

Commercial gasification of Victorian brown coal was conducted by the Gas and Fuel Corporation of Victoria between 1956 and 1969. The feedstock was briquetted coal from Yallourn open cut. The project was terminated by the availability of natural gas supplies to Melbourne. The Lurgi fixed bed, oxygen blown, pressurised gasification process was used.

There is a sound basis to believe that this process would be equally applicable to Loy Yang coal, with its good briquetting characteristics, low content of ash-forming constituents and high reactivity. However, it is important to note that fixed bed gasification of soft brown coals such as Loy Yang coal can only be conducted on dried, briquetted coal, unlike higher rank US lignites, which have been successfully gasified 'as-received' in plant trials and will be used in the Great Plains Coal Gasification Project under construction in North Dakota.

Other gasification processes involving fluid bed, entrained flow and molten bath reactors have been successfully demonstrated on soft brown coals. A major advantage of these coals which would apply to Loy Yang coal is their high reactivity, enabling lower temperature operation and higher carbon burn-out than for higher rank coals.

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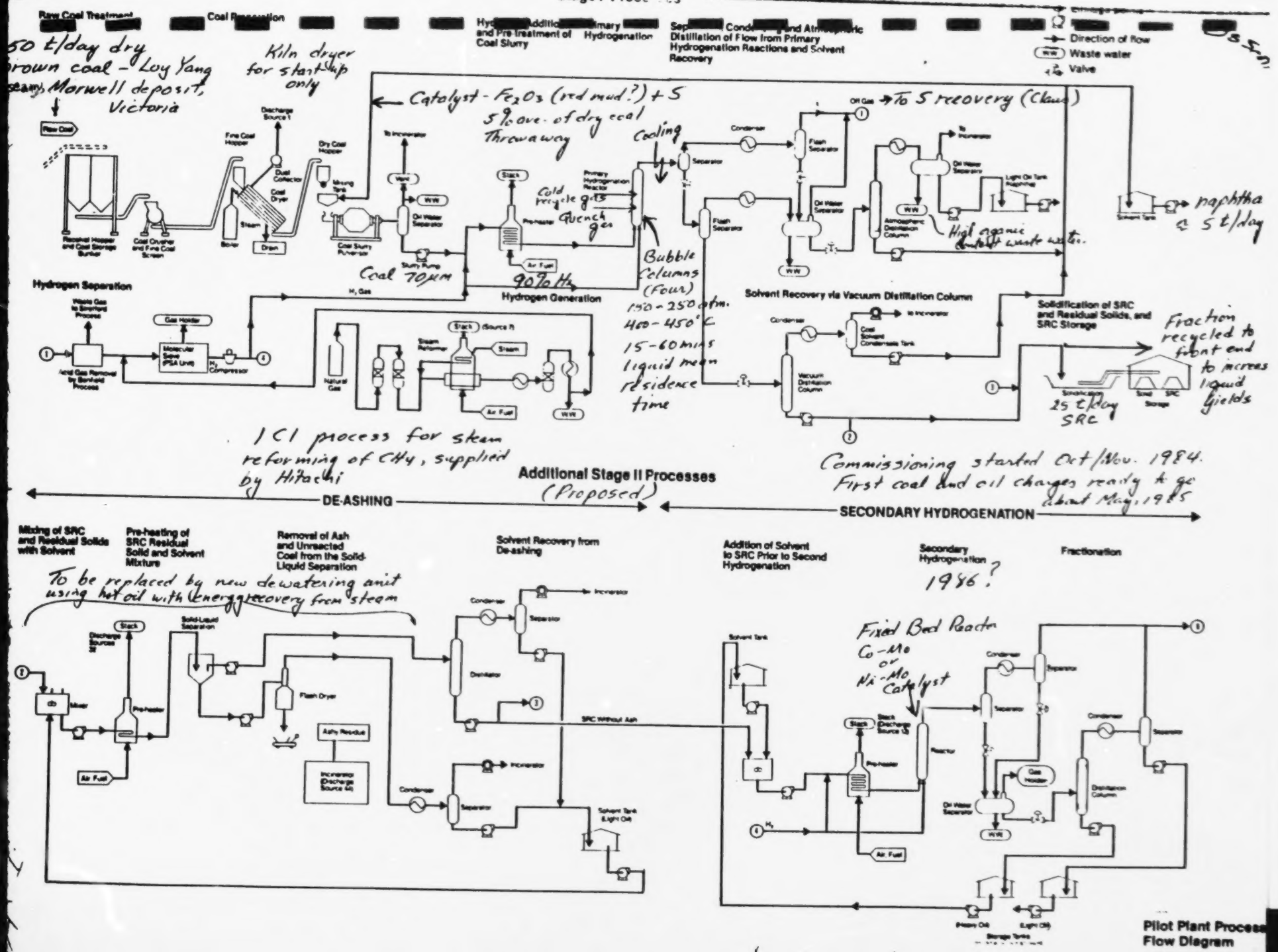
Raw Coal Treatment
Coal Preparation
Hydrogenation
Separation
Direction of flow
Waste water
Valve
50 t/day dry brown coal - Loy Yang seam, Morwell deposit, Victoria
Kiln dryer for start up only
Catalyst - Fe2O3 (red mud?) + S
5% ave. of dry coal
Throwaway
Cooling
To S recovery (Claus)
naphtha ~ 5 t/day
Coal 70 µm
90% H2
Hydrogen Generation
Hydrogen Separation
Bubble Columns (Four)
150 - 250 atm.
460 - 450°C
15 - 60 mins liquid mean residence time
Solvent Recovery via Vacuum Distillation Column
Solidification of SRC and Residual Solids, and SRC Storage
Fraction recycled to front end to increase liquid yields
25 t/day SRC
ICI process for steam reforming of CH4, supplied by Hitachi
Commissioning started Oct/Nov. 1984. First coal and oil charges ready to go about May, 1985
Additional Stage II Processes (Proposed)
DE-ASHING
SECONDARY HYDROGENATION
Mixing of SRC and Residual Solids with Solvent
Pre-heating of SRC Residual Solid and Solvent Mixture
Removal of Ash and Unreacted Coal from the Solid-Liquid Separation
Solvent Recovery from De-ashing
Addition of Solvent to SRC Prior to Second Hydrogenation
Secondary Hydrogenation
1986?
Fractionation
To be replaced by new dewatering unit using hot oil with energy recovery from steam
Fixed Bed Reactor
Co-Mo or Ni-Mo Catalyst
SRC Without Ash
Ashy Residue
Pilot Plant Process Flow Diagram